an increase in k_3^{am}. The k_2 term probably does not give a large contribution since the linear correlation shown for pyrrolidine in Figure 4 is only possible if k_2 is negligible, and this term should not be greatly affected by the structural change that is involved in going from the secondary amine to the investigated primary amines. Also, at the lower amine concentrations the first portion of the plot reported in Figure 3 for pyrrolidine is approximately linear, a condition that can only be possible if $k_{-1} > k_2 + k_3^{am}$[amine]. On comparing the above-mentioned inequalities in a simplified form (neglect of k_2), i.e.,

$$k_{-1} \ll k_3^{am}[\text{amine}] \quad \text{for cyclohexylamine}$$

$$k_{-1} \simeq k_3^{am}[\text{amine}] \quad \text{for pyrrolidine}$$

which hold at similar amine concentrations, we conclude that k_{-1}(pyrr)/k_{-1}(cyclohex) must be on the order of at least 10^2. Thus, in such a case the disappearance of base catalysis can well be caused by a decrease in k_{-1} alone.

In contrast, with other substrates such as 2,4,6-triphenylthiopyrylium, though very similar to 1, the k_{-1} (secondary amine)/k_{-1} (primary amine) ratio has been found to be lower than 14 (secondary amine = piperidine; primary amine = cyclohexylamine);[8] it should be even lower were pyrrolidine considered. An increase in k_3^{am} would then effectively contribute to the disappearance of base catalysis in the reaction of primary amines. This behavior provides further support to mechanism C because primary amines are less hindered than secondary amines and would hardly reconcile with a SB-GA mechanism because butylamine and cyclohexylamine have the same pK_a as that of pyrrolidine.

Registry No. 2,4,6-Triphenylpyrylium perchlorate, 1484-88-4; butylamine, 109-73-9; cyclohexylamine, 108-91-8; pyrrolidine, 123-75-1; piperidine, 110-89-4; morpholine, 110-91-8.

Anomaly in Palladium-Catalyzed Phenylethynylation of 2,2′-Dihalobiphenyls: Formation of Alkylidenefluorenes

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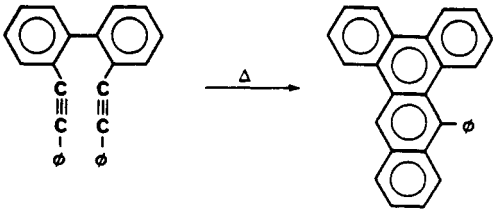
2,2′-Diiodobiphenyl and 5,5′-dinitro-2,2′-dihalobiphenyls underwent palladium-catalyzed phenylethynylation with 2 mol of phenylacetylene to yield 3-(fluoren-9-ylidene)-1,3-diphenylpropyne and 3-(3,6-dinitrofluoren-9-ylidene)-1,3-diphenylpropyne, respectively. These fluorenyl compounds exhibited well-defined splitting patterns for the fluorenyl ring protons in the 250-MHz proton NMR spectra. The structure of 3-(fluoren-9-ylidene)-1,3-diphenylpropyne was further confirmed by an independent synthesis via the thermolysis of diethyl 3-(fluoren-9-ylidene)-1,3-diphenylpropen-1-yl phosphate. The mechanistic importance of the complex iodo(fluoren-9-ylidenebenzyl)bis(triphenylphosphine)palladium(II) in the catalytic cycle was established on the basis of its reaction with phenylacetylene to give 3-(fluoren-9-ylidene)-1,3-diphenylpropyne.

The palladium-catalyzed coupling reaction[1] between an aryl halide and a terminal acetylene in the synthesis of arylalkylacetylenes,[2] tolanes,[3,4] and heteroarylacetylenes[5,6] has received considerable attention in recent years. In similar syntheses of acetylenic compounds, an alternative organocopper method[7-10] is also widely accepted. These two approaches have been shown to be superior to many tedious classical methods.[11]

We became interested in the thermally induced intramolecular cycloaddition of 2,2′-bis(phenylethynyl)biphenyl[12] (1) to a highly fused aromatic nucleus, i.e., 9-



1 2

phenyldibenz[*a*,*c*]anthracene (2).[13] Functionalization of

(1) H. A. Dieck and R. F. Heck, *J. Organometal. Chem.*, **93**, 259 (1975).
(2) K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.* 4467 (1975).
(3) L. Cassar, *J. Organomet. Chem.*, **93**, 253 (1975).
(4) K. Ishizu, U. D. G. Prabhu, D. Draney, B. H. Lee, and C. S. Marvel, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 2851 (1982).
(5) H. Yamanaka, M. Shiraiwa, K. Edo, and T. Sakamoto, *Chem. Pharm. Bull*, **27**, 270 (1979).
(6) K. Edo, H. Yamanaka, and T. Sakamoto, *Heterocycles*, **9**, 271 (1978).
(7) R. D. Stephens and C. E. Castro, *J. Org. Chem.*, **28**, 3313 (1963).
(8) R. E. Atkinson, R. F. Curtis, D. M. Jones, and J. A. Taylor, *J. Chem. Soc. C*, 2173 (1969).
(9) M. S. Shvartsberg, I. K. Kotlyarevskii, A. N. Kozhevnikova, and V. N. Andrievskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1140 (1970).
(10) M. S. Shvartsberg, L. N. Bizhan, and I. L. Kotlyarevskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1534 (1971).
(11) H. G. Viehe and V. Jäger, "Methoden der Organischen Chemie (Houben-Weyl)", Vol. V/2a, E. Müller, Ed., George Thieme Verlag, Stuggart, 1977.
(12) S. A. Kandil and R. E. Dessy, *J. Am. Chem. Soc.*, **88**, 3027 (1966).
(13) E. H. White and A. A. F. Sieber, *Tetrahedron Lett.*, 2713 (1967).

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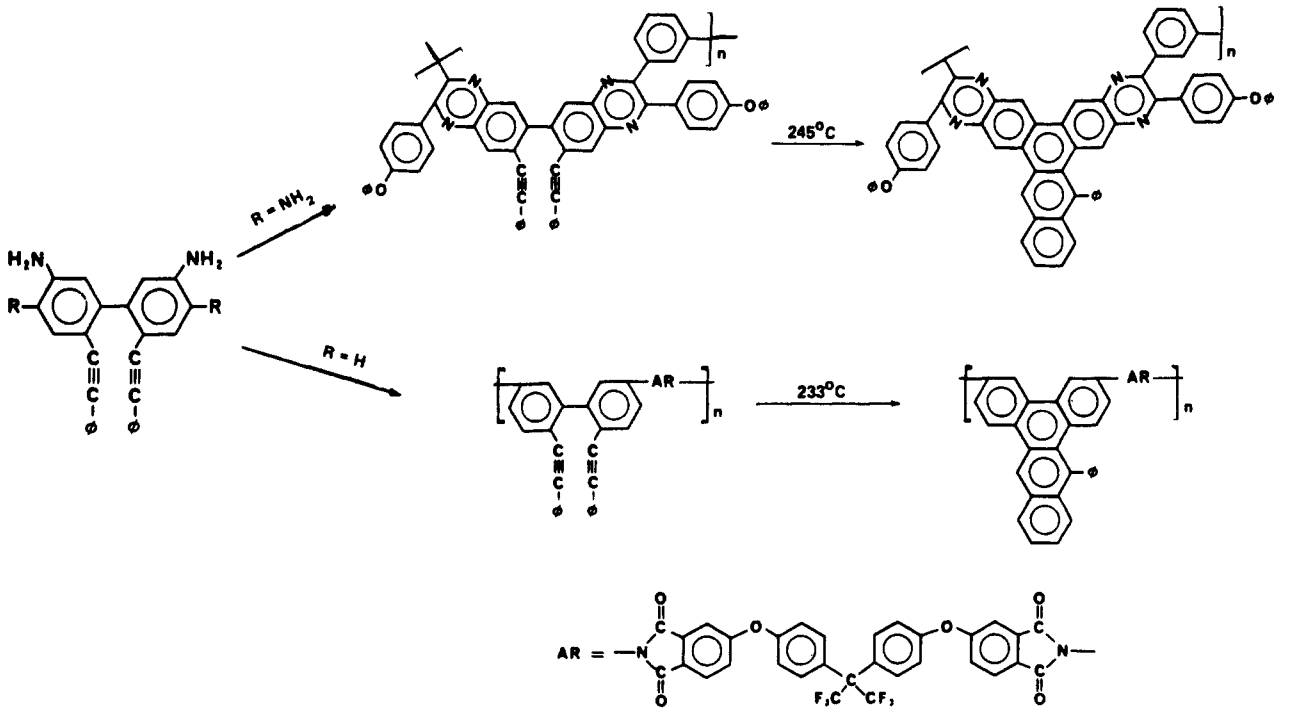
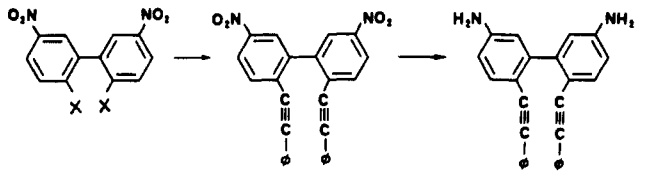
Scheme I



1 afforded the diamino[14] and the tetraamino[15] monomers which are suitable for polymerization to yield polymers containing units of 1 along the molecular backbone. These units of 1 can then undergo thermally induced intramolecular cycloaddition reactions to form the fused 9-phenyldibenz[*a*,*c*]anthracene structures. A more rigid and more thermally stable polymer having a markedly elevated glass transition temperature is eventually obtained[14,15] (see Scheme I).

Results and Discussion

Our studies required an efficient route to the synthesis of 2,2′-bis(phenylethynyl)-5,5′-diaminobiphenyl (**3**). The key step in the synthetic sequence was the double phenylethynylation of 2,2′-dihalo-5,5′-dinitrobiphenyl (**4a**, X = Br; **4b**, X = I). Stoichiometric phenylethynylation of



4a, X = Br
b, X = I

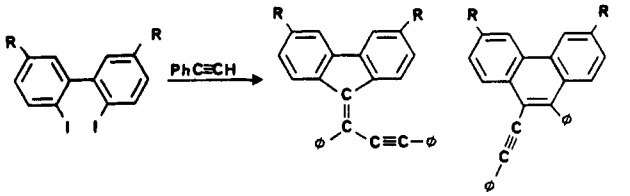
5

3

4b with cuprous phenylacetylide gave a 62% yield of 2,2′-bis(phenylethynyl)-5,5′-dinitrobiphenyl (**5**). In contrast, the dibromo compound **4a** afforded only a poor yield of **5** (21%) along with tarry intractable products.

The catalytic nature of palladium-promoted phenylethynylation of aryl halides is attractive. In principle, the presence of electron-withdrawing groups on the aryl halide facilitates the reaction.[1] Both **4a** and **4b** underwent double phenylethynylation with phenylacetylene in a 1:3 triethylamine–toluene solution at 100 °C in the presence of either a $Ph_3P/(Ph_3P)_2PdCl_2/Cu_2I_2$ catalyst system[16] or palladium acetate–tri-*o*-tolylphosphine.[17] The bright orange crystalline reaction product, however, was not the expected **5**, derived from replacement of both halogens with phenylethynyl groups, but a compound, **6**, which is an isomer of **5**.[18]

2,2′-Diiodobiphenyl underwent palladium-catalyzed phenylethynylation to give a 78% yield of a bright yellow crystalline compound (**7**) which was isomeric with 2,2′-



R = NO_2, H

6a, R = NO_2
7a, R = H

6b, R = NO_2
7b, R = H

bis(phenylethynyl)biphenyl.[12] In comparison, 2,2′-dibromobiphenyl underwent incomplete phenylethynylation with phenylacetylene in the presence of palladium acetate–tri-*o*-tolylphosphine in 1:1 triethylamine–toluene for 24 h at 90 °C.

On the basis of carbon-13 and 250-MHz proton magnetic resonance spectrometry, the products of the palladium-catalyzed double phenylethynylation of **4** and 2,2′-diiodobiphenyl have the fluorenyl structures **6a** and **7a**, respectively, rather than the phenanthrene structures **6b** and **7b**. Comparative spectra were also obtained for 9-(phenylethynyl)phenanthrene (**8**)[19] and 9-(3-phenyl-2-

(14) F. E. Arnold, U.S. Patent Appl. 678324, 19 April 1976; *Chem. Abstr.*, **86**, 73797*a* (1977); U.S. Patent Appl. 678325, 19 April 1976; *Chem. Abstr.*, **86**, 90587*z* (1977).

(15) F. L. Hedberg and F. E. Arnold, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2607 (1976).

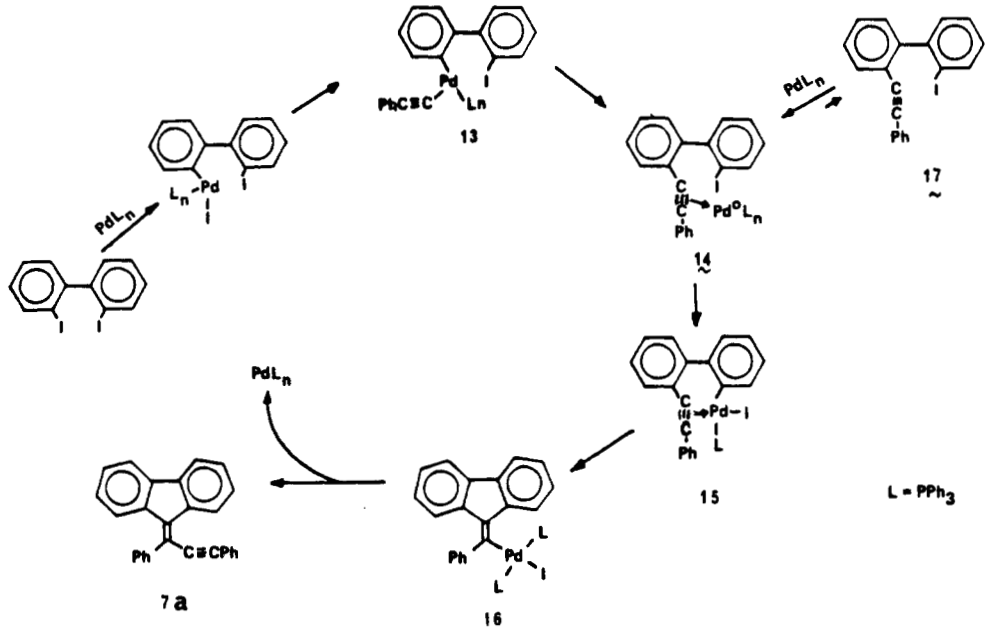
(16) E. T. Sabourin, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, 233 (1979).

(17) R. F. Heck, *Acc. Chem. Res.*, **12**, 146 (1979).

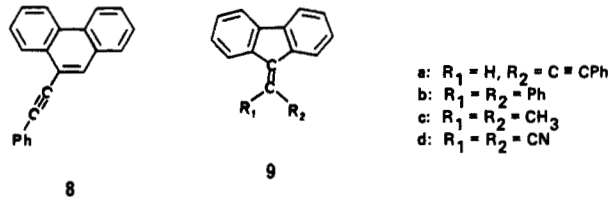
(18) Substituted 2,2′-diiodobiphenyl compounds have been reported[33] to undergo palladium-catalyzed double phenylethynylation to give the corresponding 2,2′-bis(phenylethynyl)biphenyls. Such results should be considered with caution in light of our findings.

(19) Compound **8** was synthesized by using commercially available 9-bromophenanthrene (Aldrich) as the startng material. A lithiation–iodination sequence yielded 9-iodophenanthrene (70% yield)[29] which underwent palladium-catalyzed phenylethynylation to give **8**.

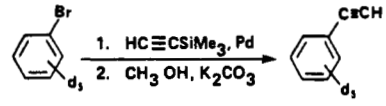
Scheme II

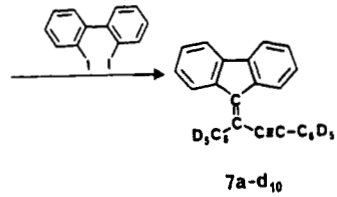


propynylidene)fluorene (**9a**).[20] Other 9-alkylidenefluorenes have been reported.[21]



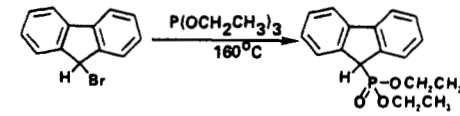
NMR Analysis of the Fluorenylidene Derivatives. Well-defined splitting patterns for the fluorenyl ring protons were observed for compounds **6a**, **7a**, and **9** in their 60-MHz proton NMR spectra. Proton NMR spectra at 250-MHz were obtained for compounds **6a** and **7a** for detailed NMR analysis. Unambiguous assignment of chemical shifts to the respective fluorenyl protons of **7a** was only possible, however, with its d_{10} analogue. In the synthesis of the d_{10} analogue, phenyl-d_5-acetylene (**10**) was

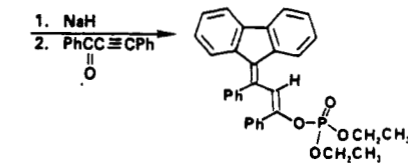




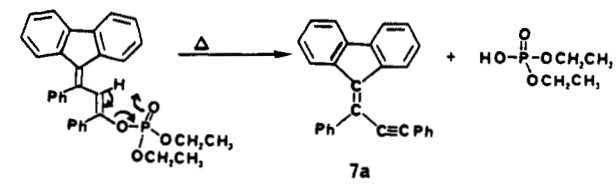
first prepared from bromobenzene-d_5. Reaction of phenyl-d_5-acetylene with 2,2′-diiodobiphenyl in the presence of palladium acetate and triphenylphosphine yielded the d_{10} derivative of **7a**. The 250-MHz proton NMR spectrum of compound **7a**-d_{10} showed only the splitting pattern of the fluorenyl protons. The chemical shift assignment was made on the basis of double resonance experiments.

Independent Synthesis of 7a. The fluorenylidene structure of **7a** was further substantiated by an independent synthetic route starting with diethyl (fluoren-9-yl)phosphonate (**11**) which was prepared by a Michaelis–Arbusov reaction.





Under the Emmons–Wadsworth conditions, the phosphonate anion of **11** underwent conjugated addition with 1,3-diphenylpropyn-3-one to yield the yellow crystalline phosphate ester **12**. On heating, **12** lost diethyl hydrogen phosphate to give bright yellow crystals, which were identified as **7a** by NMR, IR, MS, and melting point (115–116 °C).



Mechanism of Formation of 7a. The oxidative addition mechanism of the palladium-catalyzed coupling reaction (Heck reaction) of aryl halides with phenyl-

(20) Compound **9a** was previously prepared through a ring opening–homologation reaction of a dichlorocarbene adduct.[30] We synthesized compound **9a** via the Wittig reaction of the more readily available fluorenone and (3-phenyl-1,2-propadienyl)triphenylphosphonium bromide.[31]

(21) M. Rabinovitz, I. Agranat, and E. D. Bergmann, *J. Chem. Soc. B*, 1281 (1967).

(22) W. B. Austin, N. Bilow, W. J. Kelleghan, and K. S. Y. Lau, *J. Org. Chem.*, **46**, 2280 (1981).

acetylene is well-known. In the phenylethynylation reaction of 2,2′-diiodobiphenyl, the palladium(0) species generated in situ probably undergoes a similar oxidative addition with one of the two carbon-iodine bonds in 2,2′-diiodobiphenyl. The resulting arylpalladium(II) complex then undergoes nucleophilic attack by a phenylacetylide anion, which is formed from phenylacetylene in the triethylamine solvent, giving complex **13** (Scheme II).

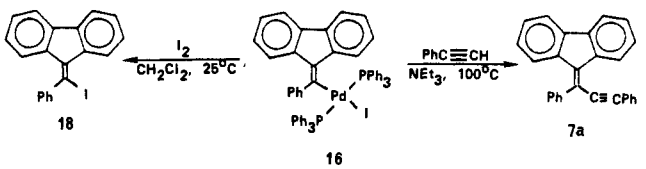
Through reductive elimination from complex **13**, carbon–carbon bond formation takes place with concomitant regeneration of palladium(0), i.e., complex **14**, which undergoes a second facile oxidative addition with the nearby carbon–iodine bond to give complex **15**. Conceivably, addition of the aryl–palladium bond in complex **15** across the carbon–carbon triple bond[23] is facilitated by the proximity of the reacting functions and also by the formation of a thermodynamically favorable five-membered ring. The resulting (fluorenylidenebenzyl)palladium(II) complex **16** further undergoes a straightforward sequence of nucleophilic attack by a phenylacetylide anion and then reductive elimination to yield the final product, i.e., compound **7a**.

When 2,2′-diiodobiphenyl was treated with 1 equiv of phenylacetylene in the presence of palladium acetate, the isolated product mixture comprised only 40% **7a** and 44% unreacted starting material. The fact that no 2-iodo-2′-(phenylethynyl)biphenyl (**17**)[24] was detected indicated that the palladium(0) complex **14**, generated from reductive elimination of complex **13**, underwent oxidative addition with the proximal carbon–iodine bond faster than dissociation to yield **17**.

The participation of complex **14** in the catalytic cycle was implicated by a separate experiment in which **17** was allowed to react with 1 equiv of phenylacetylene in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0)[25] in triethylamine. A virtually quantitative yield of fluorenyl compound **7a** was obtained.

The (fluorenylidenebenzyl)palladium(II) complex **16** was synthesized by heating **17** and tetrakis(triphenylphosphine)palladium(0) in triethylamine. Characterization of the air-stable complex **16** was accomplished by 250-MHz proton magnetic resonance spectrometry and elemental analysis. That complex **16** undergoes a reaction with phenylacetylene to yield the fluorenylidene compound **7a** clearly establishes the importance of complex **16** in the palladium-catalyzed phenylethynylation reaction of 2,2′-diiodobiphenyl.

As expected, complex **16** also undergoes electrophilic cleavage with iodine, yielding the iodo compound **18**.



18 **16** **7a**

Formation of the alkylidenefluorene skeleton, i.e., compounds **6a** and **7a**, via palladium-catalyzed double phenylethynylation of 2,2′-dihalobiphenyl suggests a facile method for attaining fluorenones and fluorenes with unusual substitution patterns. For example, 3,6-dinitrofluorenone, which cannot be synthesized by conventional nitration, can be obtained via an alkene oxidation reaction of the alkylidenefluorene **6a**.

Experimental Section

General Data. Infrared spectra were recorded on either a Beckman Acculab 6 spectrometer or a Nicolet MX-1 Fourier transform spectrometer. Liquid chromatography was performed by using a Beckman Model 345 ternary liquid chromatograph. Proton magnetic resonance spectra were recorded on either a Varian EM-360L spectrometer or a Varian FT 80-A Fourier transform spectrometer. Carbon magnetic resonance and 250-MHz proton magnetic resonance spectra were obtained by using a Bruker WM-250 Fourier transform spectrometer. Mass spectral analyses were performed by using a Finnigan OWA/1000 GC/MS spectrometer equipped with a 30-m SE-54 fused silica capillary (i.d. 0.25 mm). Microanalytical services were provided by Galbraith Laboratories, Inc., Knoxville, TN, and MicAnal Organic Microanalysis, Tucson, AZ.

2,2′-Dibromobiphenyl.[26] Into a flame-dried, 500-mL, three-necked flask equipped with an addition funnel and a low-temperature thermometer and purged with argon were placed 25.0 g (0.106 mol) of 1,2-dibromobenzene and 250 mL of anhydrous tetrahydrofuran. While the reaction mixture was cooled to −78 °C, 34.4 mL (55.0 mmol) of a 1.6 M solution of *n*-butyllithium in hexane was transferred from the stock bottle to the addition funnel by using the double-tipped needle technique. At −78 °C, dropwise addition of the lithium reagent to the substrate solution was commenced and was maintained at such a rate that the reaction temperature did not rise more than 5 °C. The entire addition required 1 h. The mixture was then warmed to 5 °C and hydrolyzed with 60 mL of 1 N aqueous hydrochloric acid. The phases were separated, and the aqueous phase was extracted four times with 50-mL portions of ether. The combined organic extracts were dried over magnesium sulfate and concentrated to a viscous oil which crystallized upon cooling. Recrystallization from absolute ethanol yielded two crops of white needles: yield 13.4 g (42.9 mmol, 80.9%); mp 79–80 °C; MS (70 eV), *m/e* 314, 312, 310 (molecular ions), 231, 233 (loss of 1 Br), 152 (base peak, loss of 2 Br); ^{1}H NMR ($CDCl_3$) δ 7.00–7.80 (complex m, aromatic).

2,2′-Diiodobiphenyl.[12] To a solution of 40.0 g (0.128 mol) of 2,2′-dibromobiphenyl in 200 mL of anhydrous ether at 0 °C was added dropwise 176 mL of a 1.6 M solution of *n*-butyllithium in hexane (0.282 mol). The mixture was stirred at 25 °C for 2 h, cooled to 0 °C, and treated with 72 g of iodine in 300 mL of anhydrous ether. At the end, the mixture acquired a brown tint, indicating a slight excess of iodine. The solution was allowed to stand 16 h at 25 °C before being washed with 300 mL each of water, 20% aqueous sodium bisulfite, saturated sodium bicarbonate, and then water. The organic phase was finally separated, dried over magnesium sulfate, and concentrated to a white solid mass. Recrystallization from methanol with charcoal treatment gave 41.5 g (0.102 mmol, 79.9%) of white rhombic crystals: mp 107–108 °C (a second recrystallization raised the melting point to 109–110 °C); ^{1}H NMR ($CDCl_3$) δ 6.96–7.56 (symmetrical m, 3 H, aromatic H_4, H_5, H_6) and 7.05 (distorted d, 1 H, J = 8.0 Hz, 1.0 Hz, aromatic H_3).

2,2′-Dibromo-5,5′-dinitrobiphenyl.[27] To a stirred solution of 6.43 g (20.6 mmol) of 2,2′-dibromobiphenyl in 25 mL of dichloromethane was added 100 mL of concentrated sulfuric acid. The mixture was cooled at 0–5 °C and then treated with dropwise addition of 30 mL of nitric acid (70% assay). The bath temperature was maintained at 0–5 °C throughout the addition. The resulting turbid yellow mixture was stirred at 25 °C for 2 h, poured into 1 L of water and extracted three times with 200-mL portions of dichloromethane. The combined organic extracts were dried over magnesium sulfate and concentrated to a yellow solid. Recrystallization from 1:3 acetone–ethanol yielded pale yellow crystals: 5.40 g (13.4 mmol, 65.2%); mp 220–221 °C; IR (KBr) 3110–3090, 1601, 1530 (intense), 1450, 1360 (intense) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 7.14 (s, 1 H, aromatic H_6) and 6.90–7.30

(23) Addition of arylpalladium across double bonds and triple bonds is well known. See H. A. Dieck and R. F. Heck, *J. Am. Chem. Soc.*, **96**, 1133 (1974). K. Kaneda, T. Uchiyama, Y. Fujiwara, T. Imanaka, and S. Teranishi, *J. Org. Chem.*, **44**, 55 (1979).

(24) The synthesis of compound **17** was an adaptation of a procedure in ref 12.

(25) D. Coulson, *Inorg. Synth.*, **12**, 112 (1972).

(26) H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 447 (1957).

(27) W. Baker, J. R. W. McOmie, D. R. Preston, and V. Rogers. *J. Chem. Soc.*, 414 (1960).

(distorted AB q, 2 H, aromatic H_3 and H_4).

The mother liquor from the recrystallization process yielded a second powdery solid which NMR showed to be 2,2′-dibromo-3,5′-dinitrobiphenyl, mp 117–119 °C.

2,2′-Diiodo-5,5′-dinitrobiphenyl. (a) Mixture of Nitronium Triflate and Hydronium Triflate as Nitrating Agent. Into a flame-dried, argon purged, three-necked flask were placed 50 mL of anhydrous dichloromethane, 4.0 mL (6.5 g) of trifluoromethanesulfonic acid, and then 1.0 mL (1.4 g) of anhydrous nitric acid (freshly distilled from sulfuric acid). The slurry was stirred at 25 °C for 30 min, cooled to 0 °C, and then treated with 3.9 g (9.6 mmol) of 2,2′-diiodobiphenyl in 20 mL of anhydrous dichloromethane. The mixture was allowed to warm to 25 °C during 2.5 h, and poured into 200 mL of water. The organic phase was separated, washed with saturated sodium bicarbonate solution (2 × 100 mL) and then with water, dried over magnesium sulfate, and concentrated to give 4.2 g (89% yield) of crude dinitro derivative. Recrystallization from 10% acetone in ethanol yielded 2.85 g (5.75 mmol, 60.0%) of pale yellow crystalline product: mp 236–238 °C; IR (KBr) 1596, 1555, 1514 (intense), 1346 (intense), 1020, 1010, 854, 832, 740 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 8.01, 8.15 (dd, 1 H, J = 8 Hz, 3 Hz, aromatic H_3) 8.30, 8.44 (dt, 1 H, J = 8 Hz, 3 Hz, 0.5 Hz, aromatic H_4), 8.15 (s, 1 H, aromatic H_6). The splitting pattern is an ABC system. Anal. Calcd for $C_{12}H_6I_2N_2O_4$: C, 29.06; H, 1.22; N, 5.65, I, 51.17. Found: C, 29.08; H, 1.32; N, 5.49; I, 51.29.

The mother liquor obtained from recrystallization contained a mixture of the 5,5′-dinitro and the 3,5′-dinitro isomers as evident from NMR and HPLC analyses.

(b) Homogeneous Nitronium Triflate Reagent. Into a flame-dried, argon-purged, three-necked flask were placed 40 mL of anhydrous dichoromethane, 3.9 mL (7.1 g, 25 mmol) of trifluoromethanesulfonic anhydride,[28] and then 1.1 mL (1.7 g) of anhydrous nitric acid. The mixture remained homogeneous. After 10 min at 25 °C, the solution was cooled to 0 °C and treated with dropwise addition of a deaerated solution of 50 g (12 mmol) of 2,2′-diiodobiphenyl in 30 mL of anhydrous dichloromethane. The reaction was allowed to proceed for 14 h at 25 °C. The mixture was then poured into 500 mL of water, and the organic phase was separated and washed with 100 mL of saturated sodium bicarbonate solution and 100 mL of water. After the mixture was dried over magnesium sulfate and the solvent removed, a pale yellow solid residue was obtained. Recrystallization from acetone–ethanol yielded pale yellow crystals: 3.8 g (7.7 mmol, 64%); mp 236–238, 239–241 C. NMR spectrometry ascertained the 5,5′-dinitro substitution pattern. High-performance liquid chromatography showed that the compound was 97% isomerically pure.

2,2′-Bis(phenylethynyl)-5,5′-dinitrobiphenyl. Reaction of 2,2′-Diiodo-5,5′-dinitrobiphenyl with Copper(I) Phenylacetylide. A mixture of 1.986 g (4.004 mmol) of 2,2′-diiodo-5,5′-dinitrobiphenyl and 1.400 g (8.509 mmol) of copper(I) phenylacetylide in 50 mL of deaerated anhydrous pyridine was heated from 25 °C to 110 °C during 1 h and kept at a gentle reflux for 16 h. The mixture was diluted by pouring it into 500 mL of 10% aqueous hydrochloric acid and extracted three times with 100-mL portions of dichloromethane–ether. The combined organic extracts were dried over magnesium sulfate and concentrated to a solid. Recrystallization from toluene gave light weight bright yellow microcrystalline needles: 1.108 g (2.50 mmol, 62.3% yield); mp 216–216.5 °C; IR (KBr) 2200, 1600, 1572, 1494, very strong and broad NO_2 absorptions at 1515, 1340, 1350 cm^{-1}; MS (70 eV), m/e 444 (molecular ion); ^1H NMR ($CDCl_3$) δ 7.30 (distorted s, 5 H, C≡CPh), 7.86 (d, 1 H, J = 9 Hz, aromatic H_3), 8.35 (dd, 1 H, J = 9 Hz, 2 Hz, aromatic H_4), 8.55 (d, 1 H, J = 2 Hz, aromatic H_6).

Phenylethynylation of 2,2′-Dibromo-5,5′-dinitrobiphenyl with Copper(I) Phenylacetylide.[7] A deaerated mixture of 2.20 g (5.47 mmol) of 2,2′-dibromo-5,5′-dinitrobiphenyl and 1.90 g (11.5 mmol) of copper(I) phenylacetylide in 50 mL of anhydrous pyridine was heated from 25 to 110 °C during 30 min and kept at 110 °C for 24 h under argon. The black mixture was diluted with an equal volume of dichloromethane and concentrated to a viscous syrup. Silica gel column chromatography yielded white crystalline 1,4-diphenylbutadiyne (mp 85–86 °C) in the hexane eluate and a yellow solid in the 1:2 dichloromethane–hexane eluate. The yellow solid was recrystallized from 1:1 hexane–benzene to give 500 mg (1.13 mmol, 20.6%) of bright yellow needlelike crystals of 2,2′-bis(phenylethynyl)-5,5′-dinitrobiphenyl, mp 216–216.5 °C. The IR and ^1H NMR spectra were superimposable on those of an authentic sample.

Palladium-Catalyzed Phenylethynylation of 2,2′-Dibromo-5,5′-dinitrophenyl. At 50 °C, a partial solution of 5.40 g (13.4 mmol) of 2,2′-dibromo-5,5′-dinitrobiphenyl and 3.00 g (29.4 mmol) of phenylacetylene in 140 mL of deaerated 3:1 toluene-triethylamine was treated with sequential addition of 25 mg (0.036 mmol) of dichlorobis(triphenylphosphine)palladium(II), 300 mg (1.15 mmol) of triphenylphosphine, and 25 mg (0.132 mmol) of copper(I) iodide. The mixture was quickly heated to 100 °C during 10 min. At this point, a clear yellow solution was obtained. After 30 min, the solution gradually changed to a red-orange color and a precipitate began to accumulate. After 2 h, the supernatant liquid turned dark reddish brown. Without cooling, the mixture was filtered. The brown solid mass was washed with boiling toluene until the solid changed into a fluffy white consistency. This white solid was soluble in cold water and had an IR spectrum superimposable on that of triethylamine hydrobromide; yield 4.40 g (92% of theory). The orange brown filtrate yielded orange-yellow crystalline material, which was recrystallized from toluene to give golden yellow needles. The product was obtained analytically pure by silica gel column chromatography with 1:1 hexane–dichloromethane as the eluant: yield 3.40 g (7.66 mmol, 57.1%); mp >310 °C; IR (KBr) 2180 (medium), very strong absorptions at 1515 and 1340 cm^{-1}; MS (70 eV), m/e 444 (molecular ion); 250-MHz ^1H NMR (pyridine-d_5, 57 °C) δ 6.79 (d, 1 H, J = 8.7 Hz, fluorenyl H_8), 7.20–7.78 (3 m, 10 H, H's on pendent phenyls), 7.90 (dd, 1 H, J = 8.7, 2.1 Hz, fluorenyl H_7), 8.48 (dd, 1 H, J = 8.6, 2.1 Hz, fluorenyl H_2), 8.89 (d, 1 H, J = 2.1 Hz, fluorenyl H_5), 8.97 (d, 1 H, J = 2.1 Hz, fluorenyl H_4), 9.14 (d, 1 H, J = 8.6 Hz, fluorenyl H_1). Anal. Calcd for $C_{28}H_{16}N_2O_4$: C, 75.67; H, 3.63; N, 6.30. Found: C, 75.59; H, 3.69; N, 6.24.

Another experiment using the same quantities of reactant, 17.63 mg of palladium(II) acetate, and 65.52 mg of tri-*o*-tolylphosphine led to the isolation of 3.20 g of the same orange-yellow crystalline product, mp >315 °C.

A further experiment using 2,2′-diiodo-5,5′-dinitrobiphenyl as the starting material gave a 68% yield of the same orange-yellow crystalline product (mp >315 °C) as above, identified by IR, MS, and NMR analyses.

Palladium-Catalyzed Phenylethynylation of 2,2′-Diiodobiphenyl. A deaerated solution of 4.060 g (10.0 mmol) of 2,2′-diiodobiphenyl and 2.261 g (22.20 mmol) of phenylacetylene in 120 mL of anhydrous triethylamine was treated with a catalyst mixture comprising 46.2 mg of dichlorobis(triphenylphosphine)palladium(II), 87.3 mg of triphenylphosphine, and 70.2 mg of copper(I) iodide. The cloudy yellow solution was stirred at 25 °C for 10 min and gradually heated to 80 °C over 30 min. At an internal temperature of 50 °C, a flocculent white precipitate began to accumulate. The mixture was maintained at 80–85 °C for 3 h, cooled, diluted with an equal volume of ether, and filtered. The recovery of white triethylamine hydroiodide was 4.123 g (90.0% of theory).

The yellow filtrate was concentrated to yield a solid residue which was recrystallized from hexane to give two crops of yellow crystals, totalling 2.757 g (7.70 mmol, 77.9%) of 3-(fluoren-9-ylidene)-1,3-diphenylpropyne. Analytically pure, brilliant yellow crystals were obtained after chromatography through a silica gel column, eluting with 2 L of 10% dichloromethane in hexane; the recovery after chromatography was 2.362 g (85.7%): mp 116–116.5 °C; IR (KBr) 2200 (weak), 1505, 1460, 790, 765, 740, 700 cm^{-1}; MS (70 eV), m/e 354 (molecular ion), 276 ($M^{+\cdot} - C_6H_5$), 252 ($M^{+\cdot} - C_6H_5C{\equiv}C$); 250-MHz ^1H NMR ($CDCl_3$) δ 6.47 (dd, 1 H, J = 0.8, 8.0 Hz, fluorenyl H_8), 6.85 (ddd, 1 H, J = 1.0, 8.0, 8.0 Hz, fluorenyl H_7), 7.18 (ddd, 1 H, J = 0.8, 7.5, 8.0 Hz, fluorenyl H_6), 7.32–7.60 (overlapping m's, 12 H, fluorenyl H_2, H_3 and phenyl H's), 7.62 (d, 1 H, J = 7.5 Hz, fluorenyl H_5), 7.68–7.70 (m, 1 H, fluorenyl H_4), 8.60–8.90 (m, 1 H, fluorenyl H_1); ^{13}C NMR ($CDCl_3$) δ 140.61, 140.56, 140.50, 140.15, 138.41, 137.78, 131.84, 129.22,

(28) K. S. Y. Lau, A. L. Landis, W. J. Kelleghan, and C. D. Beard, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 2381 (1982).

129.04, 128.70, 128.60, 127.57, 126.84, 125.71, 125.12, 123.47, 123.11, 119.63, 119.60, 102.46, 92.24. Anal. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 94.59; H, 5.36.

9-(Phenylethynyl)phenanthrene.[29] 9-Iodophenanthrene was synthesized from its bromo analogue by the conventional lithiation–iodination method. To a deaerated solution of 25.7 g (100 mmol) of 9-bromophenanthrene in 175 mL of anhydrous ether at 0 °C was added dropwise 87.0 mL of a 1.5 M *n*-butyllithium solution in hexane. The resulting mixture was kept at 0 °C for 30 min and then warmed to 25 °C. After 2 h at 25 °C, the mixture was cooled again to 0 °C and treated with a solution of 33 g of iodine in 250 mL of anhydrous ether. The mixture was warmed to 25 °C and kept at 25 °C for 2 h. The mixture was washed with 300 mL each of water, 20% sodium bisulfite solution, and then water again. The ether phase was dried over magnesium sulfate and concentrated to a solid, which was recrystallized from hexane to give fluffy crystals: 21.3 g (70.1 mmol, 70.1%); mp 92 °C (lit.[29] mp 91–92 °C); IR (KBr) weak absorptions at 1635, 1618, 1490, 1450, 1370, 1270, 1190, 900, 880, 845, and intense absorptions at 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45–7.80, 8.05–8.30, 8.40–8.65 (3 m, 8 H, aromatic H_1 to H_8), 7.39 (s, 1 H, aromatic H_9). Anal. Calcd for $C_{14}H_9I$: C, 55.29; H, 2.98; I, 41.73. Found: C, 55.10; H, 2.99; I, 41.93.

A deaerated solution of 2.49 g (8.19 mmol) of 9-iodophenanthrene in 100 mL of anhydrous triethylamine containing 22.6 mg of palladium(II) acetate, 62.1 mg of triphenylphosphine and 1.17 g (11.5 mmol) of phenylacetylene was heated to 80–85 °C for 18 h. The mixture was cooled, mixed with 100 ml of ether, and filtered to remove 1.69 g (7.38 mmol, 90.1%) of triethylamine hydroiodide.

The filtrate was washed with 100 mL each of 10% hydrochloric acid, water, saturated sodium bicarbonate solution, and water again. The organic phase was separated, dried over magnesium sulfate and concentrated. Column chromatography through silica gel eluting with hexane yielded an off-white light weight fibrous solid: yield 1.00 g (3.60 mmol, 44.0%); mp 114–114.5 °C; IR (KBr) 3070, 1600, 1495, 1455, 1445, 1425, 1385, 745 cm^{-1}; MS (70 eV), *m/e* 278 (molecular ion); ^1H NMR ($CDCl_3$) δ 7.32–7.45 (m, 10 H, phenanthryl H_2–H_8 and phenyl H_3, H_4, H_5 protons), 8.10 (s, 1 H, phenanthryl H_9) and 8.45–8.90 (m, 3 H, phenanthryl H_1 and phenyl H_2, H_6); ^{13}C NMR ($CDCl_3$) δ 132.00, 131.90 (2), 131.44, 131.32, 130.46, 130.31, 128.70, 128.64 (2), 127.58, 127.21, 127.09, 123.61, 122.96, 122.77, 119.82, 94.18, 88.03. Anal. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 94.73; H, 5.07.

9-(3-Phenyl-2-propynylidene)fluorene.[30] To a Schlenk tube charged with 3.77 g (8.25 mmol) of (3-phenyl-1,2-propadienyl)-triphenylphosphonium bromide[31] in 50 mL of anhydrous tetrahydrofuran (THF) at −78 °C was added 11.0 mL of a 1.0 M solution of *n*-butyllithium in hexane. The mixture was stirred at −78 °C for 30 min and was treated by dropwise addition of a solution of 1.30 g (7.22 mmol) of 9-fluorenone in 10 mL of anhydrous THF. The resulting mixture was stirred at −78 °C for another 30 min and then warmed to 25 °C during 1 h.

Thin-layer chromatography (silica gel plate, hexane eluant) of the reaction mixture indicated the presence of two products in addition to triphenylphosphine oxide and unreacted fluorenone. The reaction mixture was stirred for 30 h at 25 °C and then heated at reflux for 2 h. The progress was followed by thin-layer chromatography at appropriate intervals. No appreciable change from the results of the initial thin layer chromatography was apparent. The mixture was worked up by diluting with 100 ml of 10% hydrochloric acid and extracting with ether (3 × 50 mL). The combined ether extracts were dried over magnesium sulfate and concentrated to an oil. Chromatographic separation through a silica gel column by elution with hexane gave two fractions of 200 mL each.

Fraction 1 contained 100 mg (0.455 mmol, 6.30%) of 9-(1-butylidene)fluorene: mp 49–50 °C; MS (70 eV), *m/e* 220 (molecular ion); ^1H NMR ($CDCl_3$) δ 1.05 (distorted t, 3 H, J = 7.0 Hz, CH_3), 1.70 (br sextet, 2 H, J = 7.0 Hz, $CH_2CH_2CH_3$), 2.77 (q, 2 H, J = 7.0 Hz, $CH_2CH_2CH_3$), 6.50 (t, 1 H, J = 7.0 Hz, vinylic), 7.13–7.40, 7.47–8.00 (2 m, 8 H, aromatic).

Fraction 2 contained the desired 9-(3-phenyl-2-propynylidene)fluorene: 72.0 mg (0.271 mmol, 3.75%); IR (KBr) 3060, 2180, 1620, 1600, 1490, 1445, 772, 752, 728, 690 cm^{-1}; MS (70 eV), *m/e* 266 (molecular ion); 250-MHz ^1H NMR ($CDCl_3$) δ 6.88 (s, 1 H, vinyl), 7.38–7.55 (overlapping m, 7 H, fluorenyl H_2, H_3, H_6, H_7 and phenyl H_3, H_4, H_5), 7.69–7.75 (m, 2 H, fluorenyl H_4, H_5), 7.74–7.85 (m, 3 H, fluorenyl H_8 and phenyl H_2, H_6), 8.66–8.74 (m, 1 H, fluorenyl H_1); ^{13}C NMR ($CDCl_3$) δ 144.60, 141.10, 139.72, 138.60, 137.33, 131.94, 129.56, 129.35 (2), 129.09, 128.86 (2), 127.72, 127.44, 125.25, 123.67, 120.60, 120.12, 119.98, 103.94, 101.12, 88.96.

Phenyl-d_5-acetylene. A deaerated solution of 19.85 g (122.6 mmol) of bromobenzene-d_5 and 18.00 g (183.7 mmol) of ethynyltrimethylsilane in 50 mL of anhydrous triethylamine was treated with 30 mg of palladium(II) acetate and 100 mg of triphenylphosphine. The mixture was heated at 100 °C under argon for 24 h, cooled to 25 °C, diluted with an equal volume of ether, and filtered. The recovery of the triethylamine hydrobromide (7.418 g, 40.76 mmol) indicated only a 33.2% conversion had been realized.

The brown filtrate was concentrated to an oil and passed through a short column of silica gel, eluting with 100 mL of hexane. The eluate was concentrated to a pale yellow oil. Distillation of the oil under reduced pressure gave two fractions. Fraction 1 [bp 40–50 °C (8 torr)] was recovered bromobenzene-d_5. Fraction 2 [bp 53–60 °C (1 torr)] was an orange-yellow viscous oil identified as (phenyl-d_5-ethynyl)trimethylsilane: yield 7.055 g (39.41 mmol, 32.2% based on original amount of bromobenzene-d_5 or 96.7% based on % conversion); IR (film) 2980, 2300, 2175, 1270, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20.

The silane was dissolved in 25 mL of anhydrous methanol and treated with 100 mg of anhydrous potassium carbonate. The mixture was stirred under argon at 25 °C for 5 h. The solvent was removed, and the residue was taken up in 50 mL of ether and extracted with 50 mL of water. The ether portion was separated, dried over magnesium sulfate, and concentrated by distilling off the solvent. The residual oil was then distilled at 1 torr into a cold trap chilled at −78 °C. The yield was virtually quantitative. Identification of the product as the expected phenyl-d_5-acetylene was based on its IR (3300, 2300, 2175 cm^{-1}) and ^1H NMR (in $CDCl_3$, singlet at δ 3.08) spectra.

Palladium-Catalyzed Reaction of 2,2′-Diiodobiphenyl with Phenyl-d_5-acetylene. A deaerated mixture of 650 mg (1.60 mmol) of 2,2′-diiodobiphenyl, 420 mg (3.93 mmol) of phenyl-d_5-acetylene, 10 mg of palladium(II) acetate, and 50 mg of triphenylphosphine in 25 mL of anhydrous triethylamine was heated under argon at 100 °C for 24 h. The mixture was then cooled, mixed with an equal volume of ether, and filtered to remove 682 mg (2.98 mmol, 93.1% of theory) of triethylamine hydroiodide. The filtrate was concentrated and purified by column chromatography through silica gel. Fraction 1 (500 mL of hexane) yielded 340 mg of crystalline 1,4-diphenylbutadiyne, mp 85–86 °C. Fraction 2 (500 mL of hexane) contained a trace amount of oily material which was not characterized. Fraction 3 (500 mL of hexane) contained a trace quantity of a mixture and was discarded. Fraction 4 (1 L of hexane) yielded 65 mg (0.18 mmol, 11.2%) of a crystalline yellow solid, which was identified as the d_{10} analogue of 3-(fluoren-9-ylidene)-1,3-diphenylpropyne: mp 114 °C; IR (KBr) 3060, 2270, 2180, 1575, 1495, 785, 730 cm^{-1}; the 250-MHz ^1H NMR spectrum showed that the splitting patterns of the protons were identical with those of the fluorenyl protons of the undeuterated compound, 3-(fluoren-9-ylidene)-1,3-diphenylpropyne. Double-resonance NMR experiments performed on this deuterated compound unequivocally established the chemical shift for each and every proton on the fluorenyl skeleton.

Diethyl (Fluoren-9-yl)phosphonate. A mixture of 4.70 g (19.2 mmol) of 9-bromofluorene and 3.50 g (2.11 mmol) of triethyl phosphite was heated at 160 °C for 1 h. The oil was passed through a short silica gel column, eluting with hexane. The filtrate was evaporated to dryness to yield 3.70 g (12.3 mmol, 64.1%) of diethyl (fluoren-9-yl)phosphonate as a colorless oil: IR (film) 3010, 1490, 1460, 1260, 1175, 1060, 1040, 975 cm^{-1}; ^1H NMR ($CDCl_3$)

(29) M. A. Goldberg, E. P. Ordas, and G. Carsch, *J. Am. Chem. Soc.*, **69**, 260 (1947). 9-Iodophenanthrene was obtained in 45% yield from its amino precursor.

(30) E. Wada, S. Fujisaki, A. Nakashima, and S. Kajigaeshi, *Bull. Chem. Soc. Jpn.*, **48**, 739 (1975).

(31) H. Saikachi, N. Shimojyo, and H. Ogawa, *Yakugaku Zasshi*, **90**, 581 (1970); *Chem. Abstr.*, **73**, 35456*n* (1970).

δ 1.07 (t, J = 7.0 Hz, 6 H, OCH_2CH_3), 2.34 (2 overlapping q's, J = 7.0 Hz, 4 H, $OCH_AH_BCH_3$), 4.27, 4.78 (d, 1 H, J_{PCH} = 31.0 Hz, fluorenyl H_9), 7.30–7.53 and 7.70–8.10 (2 m, aromatic).

Diethyl 3-(Fluoren-9-ylidene)-1,3-diphenylpropen-1-yl Phosphate. To a slurry of 400 mg of a 50% oil dispersion of sodium hydride (8.33 mmol) in 15 mL of anhydrous tetrahydrofuran (THF) at 0 °C was added a solution of 2.00 g (6.62 mmol) of diethyl (fluoren-9-yl)phosphonate in 10 mL of anhydrous THF. Gas evolution was instantaneous. After 30 min, a solution of 1.50 g (7.28 mmol) of 1,3-diphenylpropynone[32] in 10 mL of anhydrous THF was added. The mixture turned dark red and was heated at reflux for 2 h.

The mixture was then cooled to 25 °C and diluted with 100 mL of water. The yellow light weight solid was isolated by filtration and air-dried. Purification by filtration through neutral alumina followed by recrystallization from hexane gave 3.33 g (6.56 mmol, 99.0%) of yellow crystals of *cis,trans*-diethyl 3-(fluoren-9-ylidene)-1,3-diphenylpropen-1-yl phosphate: mp 146–150 °C; IR (KBr) 3080, 3000, 2940, 1605, 1580, 1460, 1070, 1040, 780 cm^{-1}; MS (70 eV), m/e 508 (molecular ion), 354 ($M^+ - (CH_3CH_2O)_2P(O)OH$, base peak); 250-MHz ^1H NMR ($CDCl_3$) δ 1.00 (overlapping t's, 6 H, OCH_2CH_3), 3.50–4.50 (overlapping q's, 4 H, $OCH_AH_BCH_3$), 6.40 (d, 1 H, fluorenyl H_8), 6.80 (td, 1 H, fluorenyl H_7), 7.00 (distorted td, 1 H, fluorenyl H_6), 7.06–7.20, 7.25–7.40, 7.44–7.65 (3 sets of m's, 14 H, phenyl protons and fluorenyl H_2, H_3, H_4, H_5), 8.17–8.27 (m, 1 H, fluorenyl H_1), 11.0 (br s, 1 H, hydrogen bonded vinyl H). Anal. Calcd for $C_{32}H_{29}O_4P$: C, 75.63; H, 5.75; P. 6.09. Found: C, 75.86; H, 5.92; P, 6.27.

Thermal Decomposition of Diethyl 3-(Fluoren-9-ylidene)-1,3-diphenylpropen-1-yl Phosphate. A deaerated solution of 1.00 g (1.97 mmol) of diethyl 3-(fluoren-9-ylidene)-1,3-diphenylpropen-1-yl phosphate in 20 mL of *N,N*-dimethylacetamide was heated at 140 °C for 4 h. Thin-layer chromatography (silica gel plate, 1:1 dichloromethane–hexane) showed the presence of starting material and a new yellow component.

Heating at 120 °C for 100 h did not seem to effect complete conversion, as judged by the persistent presence of the starting material on the thin-layer chromatogram.

The mixture was diluted with 100 mL of water and extracted with ether (2 × 50 mL). The combined ether extracts were dried over magnesium sulfate and concentrated to a brown gummy solid.

Column chromatography through silica gel, eluting with 1:4 dichloromethane–hexane, yielded 70.1 mg (0.198 mmol, 10.1%) of 3-(fluoren-9-ylidene)-1,3-diphenylpropyne: mp 115–116 °C; IR and ^1H NMR spectra were superimposable on those of an authentic sample.

2-Iodo-2′-(phenylethynyl)biphenyl.[12] A deaerated slurry of 6.726 g (16.57 mmol) of 2,2′-diiodobiphenyl and 2.690 g (17.40 mmol) of copper phenylacetylide in 100 mL of anhydrous pyridine was heated at reflux (115 °C) under nitrogen. Initially, the slurry was bright yellow. After 1 h, it became a brown solution. The brown solution was heated for an additional 17 h, cooled to 25 °C, and diluted with an equal volume of water. The precipitate that formed was taken up in 100 mL of dichloromethane. The organic phase was separated, and the blue aqueous phase was extracted twice with 50-mL portions of dichloromethane. The combined organic extracts were dried over magnesium sulfate, filtered, and evaporated to dryness.

Thin-layer chromatography (silica gel plate, 1:2 dichloromethane–hexane) revealed the presence of four components. Column chromatography through a silica gel column afforded eight 1-L fractions. Fraction 1 (hexane eluant) yielded 2.022 g (4.980 mmol, 30.1% recovery) of 2,2′-diiodobiphenyl, mp 107–108 °C. Fractions 2–4 (hexane eluant) yielded a total of 2.622 g (6.900 mmol, 41.7%) of the desired 2-iodo-2′-(phenylethynyl)biphenyl, mp 81–82 °C. Fraction 5 (hexane eluant) yielded 55 mg (0.17 mmol, 1.0%) of 9-phenyldibenz[a,c]anthracene, mp 231–232 °C. Fraction 6 (hexane eluant) yielded 606 mg (1.71 mmol, 10.3%) of 2,2′-bis(phenylethynyl)biphenyl, mp 118–119 °C. Fractions 7 and 8 (1:2 dichloromethane–hexane) yielded only trace amounts of impure solids and were discarded.

(32) Y. Tohda, K. Sonogashira, and N. Hagihara, *Synthesis*, 777 (1977).

(33) R. L. Frentzel and C. S. Marvel, *J. Polym. Sci., Polym. Chem. Ed.*, 17, 1073 (1979).

2-Iodo-2′-(phenylethynyl)biphenyl: mp 81–82 °C; IR (KBr) 3060, 2220, 1600, 1496, 1459, 1442, 1428, 1107, 1000, 755, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.85–7.70 (complex m, 12 H, aromatic), 7.92, 8.05 (br d, 1 H, aromatic H_3 on biphenyl unit). Anal. Calcd for $C_{29}H_{13}I$: C, 63.18; H, 3.45; I, 33.38. Found: C, 63.00; H, 3.53; I, 33.11.

9-Phenyldibenz[a,c]anthracene: mp 231–232 °C (lit.[12] mp 235–236 °C); IR (KBr) weak absorptions at 3060, 1600, 1490, 1445, 1365, intense absorptions at 760, 720, 705 cm^{-1}. Anal. for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 94.61; H, 5.22.

2,2′-Bis(phenylethynyl)biphenyl: mp 118–119 °C; IR (KBr) 3060, 2220 (weak), 1600, 1495, 1440, 755 (intense), 690 cm^{-1} (intense); 250-MHz ^1H NMR ($CDCl_3$) δ 7.22 (br s, 10 H, H's on pendent phenyls), 7.37–7.41 (m, 4 H, biphenylyl H_4, $H_{4'}$, H_5, $H_{5'}$), 7.52–7.56 (m, 2 H, biphenylyl H_6, $H_{6'}$), 7.63–7.65 (m, 2 H, biphenylyl H_3, $H_{3'}$); ^{13}C NMR ($CDCl_3$) δ 143.41, 132.19, 131.55 (2), 130.52, 128.35 (2), 128.17, 127.85, 127.61, 123.73, 123.08, 92.74, 89.36. Anal. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 95.19; H, 5.27.

Palladium-Catalyzed Phenylethynylation of 2-Iodo-2′-(phenylethynyl)biphenyl. A pale yellow solution of 800 mg (2.11 mmol) of 2-iodo-2′-(phenylethynyl)biphenyl and 235 mg (2.30 mmol) of freshly distilled phenylacetylene in 13 mL of deaerated anhydrous triethylamine (Fluka reagent grade) was stirred at 25 °C under nitrogen while 20 mg of triphenylphosphine and 10 mg of tetrakis(triphenylphosphine)palladium(0) were added. The mixture was stirred for another 5 min and then heated to 100 °C over 15 min. After 1 h at 100 °C, a copious white precipitate was obtained, and the supernatant solution became bright yellow. The slurry was cooled to 25 °C under argon and filtered to remove 390 mg of triethylamine hydroiodide. On being chilled, the filtrate yielded a second crop of the hydroiodide (40 mg).

The filtrate was evaporated to dryness, leaving a yellow solid mass. Thin-layer chromatography on silica gel indicated the presence of one yellow component. The solid, in hexane, was passed through a short silica gel column and recrystallized twice from hexane: yield 710 mg (2.01 mmol, 95.1%); mp 115–116 °C; the IR and ^1H NMR spectra were superimposable on those of authentic 3-(fluoren-9-ylidene)-1,3-diphenylpropyne.

Reaction of 2,2′-Diiodobiphenyl with 1 Equiv of Phenylacetylene under Palladium Catalysis. A pale yellow solution of 4.063 g (10.00 mmol) of 2,2′-diiodobiphenyl and 1.020 g (10.00 mmol) of freshly distilled phenylacetylene in 100 mL of deaerated anhydrous triethylamine (Fluka reagent grade) was warmed to 50 °C under argon. The catalyst (50 mg of triphenylphosphine and 20 mg of palladium(II) acetate) was added. The mixture was brought to 90 °C over 15 min. Precipitation commenced, and the reaction mixture was stirred at 90 °C for 21 h. The slurry was cooled under argon and diluted with 100 mL of ether. The white insoluble triethylamine hydroiodide was filtered off (2.12 g, 92.5% recovery). The orange yellow filtrate was concentrated and dissolved in 200 mL of ether. The organic solution was washed with 200 mL of 10% aqueous hydrochloric acid, 200 mL of saturated sodium bicarbonate, and then with water. After being dried over magnesium sulfate, the solution was concentrated.

High-performance liquid chromatography of the crude product indicated the presence of 2,2′-diiodobiphenyl (44.9%), 3-(fluoren-9-ylidene)-1,3-diphenylpropyne (44.3%) and a third component (ca. 10.8%).

Column chromatography (silica gel) of the crude product mixture yielded three fractions. Fraction 1 (hexane eluant) was found to contain 1.784 g (4.394 mmol, 43.9% recovery) of 2,2′-diiodobiphenyl (mp 108–109 °C). Fraction 2 (hexane eluant) contained a trace amount of an oil which was not characterized. Fraction 3 (1:4 dichloromethane–hexane eluant) contained 1.021 g (2.88 mmol, 28.8% isolated yield) of 3-(fluoren-9-ylidene)-1,3-diphenylpropyne, which was identified by its melting point (115–116 °C) and mixture melting point with an authentic sample.

Reaction of 2-Iodo-2′-(phenylethynyl)biphenyl with Tetrakis(triphenylphosphine)palladium(0) in Triethylamine at Reflux. A brownish yellow slurry of 381 mg (1.00 mmol) of 1-iodo-2′-(phenylethynyl)biphenyl and 1.152 g (0.998 mmole) of tetrakis(triphenylphosphine)palladium(0) in 13 mL of deaerated anhydrous triethylamine was heated at a gentle reflux (oil bath at 100 °C) under nitrogen for 1.5 h. The solid in the slurry appeared to be more copious and a lighter yellow than at the start.

The mixture was cooled, diluted with 50 mL of ether, and filtered to give a yellow powdery solid.

The yellow orange filtrate was evaporated to dryness to give a solid mass. Thin-layer chromatography (silica gel plate) indicated triphenylphosphine was the predominant component. Several other components were present in trace quantities.

The yellow powdery solid isolated from the reaction was identified as iodo(fluoren-9-ylidenebenzyl)bis(triphenylphosphine)palladium(II): yield 981 mg (0.970 mmol, 97.2%); mp 204–206 °C; IR (KBr) 3050, 1570, 1481, 1435, 1085, 780, 740, 730, 690 cm^{-1}; 250-MHz ^1H NMR ($CDCl_3$) δ 6.36 (d, 1 H, J = 7.5 Hz, fluorenyl H_8), 6.48 (br d, 2 H, J = 7.5 Hz, fluorenyl H_2, H_7), 6.65 (ddd, 1 H J = 7.5, 7.5, 1.0 Hz, fluorenyl H_6), 6.84–7.67 (3 sets of multiplets, 38 H, fluorenyl H_3, H_4, H_5 and all phenyl H's), 9.83–9.87 (m, 1 H, fluorenyl H_1). Anal. for $C_{56}H_{43}IP_2Pd$: C, 66.52; H, 4.29; I, 12.55. Found: C, 66.39; H, 4.29; I, 12.67.

Reaction of Phenylacetylene with Iodo(fluoren-9-ylidenebenzyl)bis(triphenylphosphine)palladium(II). A mixture of 401 mg (0.397 mmol) of iodo(fluoren-9-ylidenebenzyl)bis(triphenylphosphine)palladium(II) and 55 mg (0.54 mmol) of phenylacetylene in 10 mL of deaerated, anhydrous triethylamine (Fluka reagent grade) was heated at 100 °C under nitrogen for 10 min. At this point, the yellow complex turned black.

The mixture was cooled, diluted with 50 mL of ether, and filtered. Unreacted starting yellow complex was isolated (214 mg; i.e., the reaction was ca. 50% over in 10 min).

The black filtrate was concentrated to give a brown mass. Thin-layer chromatography (silica gel plate) indicated the presence of bright yellow 3-(fluoren-9-ylidene)-1,3-diphenylpropyne. Column chromatography through silica gel, eluting with 1:4 dichloromethane–hexane (1 L), removed a bright yellow band. Evaporation of the eluate to dryness, followed by recrystallization of the solid from hexane, gave bright yellow crystals of 3-(fluoren-9-ylidene)-1,3-diphenylpropyne: yield 30 mg (0.085 mmol, 21%); mp 114–116 °C; IR and ^1H NMR spectra were superimposable on those of an authentic sample.

Reaction of Iodine with Iodo(fluoren-9-ylidenebenzyl)bis(triphenylphosphine)palladium(II). A solution of 204 mg (0.202 mmol) of iodo(fluoren-9-ylidenebenzyl)bis(triphenylphosphine)palladium(II) in 50 mL of anhydrous dichloromethane was treated with dropwise addition of a 0.134 N solution of iodine in dichloromethane (standardized against sodium thiosulfate). At the end point, the purple color of iodine persisted. The mixture was then diluted with an equal volume of hexane and filtered to remove the orange-yellow diiodobis(triphenylphosphine)palladium(II) complex: mp 263–264 °C.

The filtrate was concentrated. Thin-layer chromatography on a silica gel plate indicated the presence of one product. Column chromatography through silica gel, eluting with hexane, yielded analytically pure needles of (α-iodobenzylidene)fluorene: 11.5 mg (0.030 mmol, 15.0%), mp. 137–138 °C; IR (KBr) weak absorptions at 3050, 1610, 1572, and strong absorptions at 1444, 778, 726 cm^{-1}; GC/MS indicated 99+% purity and a molecular ion at m/e 380; 250-MHz ^1H NMR ($CDCl_3$) δ 6.09 (dd, 1 H, J = 8.2, 0.8 Hz, fluorenyl H_8), 6.81 (ddd, 1 H, J = 8.2, 8.2, 0.8 Hz, fluorenyl H_7), 7.21 (ddd, 1 H, J = 8.2, 7.5, 0.8 Hz, fluorenyl H_6), 7.63 (dd, 1 H, J = 7.5, 0.8 Hz, fluorenyl H_5), 7.71 (m, 1 H, fluorenyl H_4), 7.33–7.73 (complex m, 7 H, fluorenyl H_2, H_3 and phenyl H's), 9.04–9.08 (m, 1 H, fluorenyl H_1); ^{13}C NMR ($CDCl_3$) δ 147.84, 142.03, 141.06, 139.68, 138.82, 138.41, 129.73, 129.38, 128.96, 128.46, 127.86, 127.16, 126.67, 125.54, 125.04, 119.80, 119.19, 99.46. Anal. Calcd for $C_{20}H_{13}I$: C, 63.18; H, 3.45; I, 33.38. Found: C, 63.25; H, 3.34; I, 33.45.

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Registry No. **4a**, 52026-22-9; **4b**, 61837-21-6; **5**, 61837-22-7; **6a**, 87682-41-5; **7a**, 87682-42-6; **7a**-d_{10}, 87682-43-7; **8**, 87682-44-8; **9a**, 56150-56-2; **10**, 25837-46-1; **11**, 7142-76-9; **12**, 87682-45-9; **16**, 87682-40-4; **17**, 10271-61-1; **18**, 87682-46-0; PhC≡CH, 536-74-3; HC≡CSiMe$_3$, 1066-54-2; 1,2-dibromobenzene, 583-53-9; 2,2′-dibromobiphenyl, 13029-09-9; 2,2′-diiodobiphenyl, 2236-52-4; 2,2′-dibromo-3,5′-dinitrobiphenyl, 87682-47-1; copper(I) phenylacetylide, 13146-23-1; 9-bromophenanthrene, 573-17-1; 9-iodophenanthrene, 17024-12-3; (3-phenyl-1,2-propadienyl)triphenylphosphonium bromide, 64934-32-3; 9-fluorenone, 486-25-9; 9-(1-butylidene)fluorene, 29754-40-3; bromobenzene-d_5, 4165-57-5; (phenyl-d_5-ethynyl)trimethylsilane, 87682-48-2; 1,3-diphenylpropyn-3-one, 7338-94-5.

A Convenient Synthesis of (Acyloxy)alkyl α-Ethers of Phenols

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(Acyloxy)alkyl α-ethers (1) of phenols, thiophenol, and catechols have been prepared in good yield by their alkylation with (acyloxy)alkyl α-chlorides or iodides in acetone in the presence of K_2CO_3. In addition, one example of an (acylthio)alkyl α-ether was prepared. Either partial or complete acylation rather than alkylation on oxygen took place if the α-iodide was not used except for reactions of 3-chloro-1(3*H*)-isobenzofuranone with phenol or catechol or the reaction of (benzoylthio)methyl chloride with β-estradiol. It is suggested that more alkylation takes place with iodide as a leaving group because of the tighter transition state that develops with the better nucleofuge. The alkylation reaction sequence has two advantages for the synthesis of 1: (1) the mildness of the reaction conditions and (2) the wide variety of acyl and alkyl groups that can be incorporated into the product through the (acyloxy)alkyl α-halides.

Background

(Acyloxy)alkyl α-ethers of phenols (1) have been studied because of their similarity to proposed intermediates in enzymatic reactions[1] and because of their potential use as pesticides.[2,3] However, the fact that (acyloxy)alkyl de-

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