Intramolecular Organometal–Acetylene and Acetylene–Acetylene Interactions. Routes to Benzylidenefluorene and C$_4$ Ring Systems

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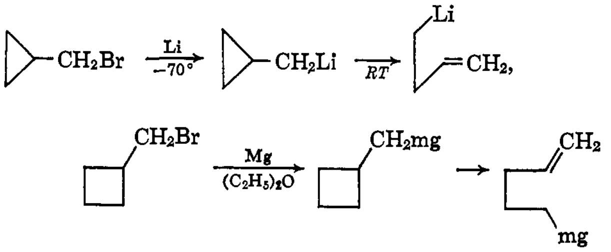
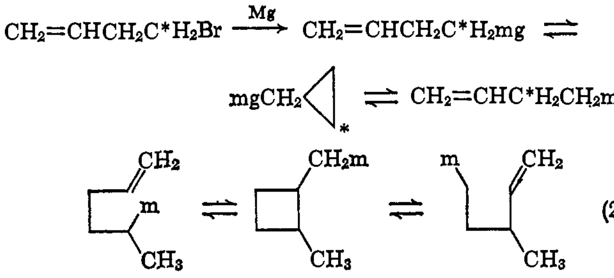
Abstract: Cyclopropylcarbinyl and cyclobutylcarbinyllithium reagents are known to undergo facile *ring opening* to open-chain analogs (eq 1 and 2). A systematic study of intramolecular metal–acetylene interactions schematically shown as cases I–III has been made, and both carbanionic and radical *ring closures* to five-membered ring aromatic carbocyclic organometallics have been observed with lithium and copper, respectively. Magnesium derivatives may also lead to ring closure processes, depending upon the array angle. Where possible closures to a four-membered ring, or closure to a six-membered ring in competition to closure to a five-membered ring can occur, these do not take place. An acetylene–acetylene interaction leading to a C$_4$ ring system is presented.

Several groups of investigators[1-3] have shown during the past 5 years that cyclopropyl- and cyclobutylcarbinylmagnesium or -lithium compounds are unstable undergoing facile ring opening to the allylcarbinyl and 4-pentenylmetal system (eq 1). These processes involve equilibria as shown by skeletal and isotopic labeling experiments. The latter indicate that intramolecular addition of organolithium or organomagnesium reagents to olefins can occur. The position of equilibria in the above cases, lying largely if not entirely toward that of the open-chain hydrocarbon, is felt to involve ring strain factors. Roberts has reported on the norbornenyl–nortricyclyl–magnesium bromide equilibrium, where *ring-closed* product predominates. It would seem most logical to pursue this concept, which thus far has been of mechanistic interest, into the realm of synthetic chemistry. In particular, the placing in close proximity of an organometallic moeity and an acetylenic bond, such that intramolecular addition might lead to four-, five-, or six-membered rings, would seem of interest. The report of Letsinger[4] and Castro[5] on intramolecular ring closures leading to heterocyclic ring systems from precursors having properly oriented nucleophiles and acetylenic linkages is encouraging. The present paper deals with three geometrical arrays of the organometallic unit (C—m) and the acetylene.



(1)



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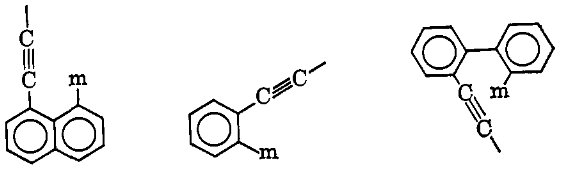

case I

case II

case III

Case I involves an array angle of 0°, and has been previously reported on in part.[6] Case II involves a diverging array angle of 60°. Case III involves a converging angle of 60° (with the biphenyl nucleus conformer with maximum interaction). Three types of metal–acetylene interactions were probed: (A) those in which the C—m linkage is predominantly ionic (M—Li, Mg) providing incipient carbanions, (B) those in which decomposition of the C—m linkage to radicals is known or suspected (M=Cu), and (C) those in which covalent bonding in the C—m unit predominates (M=Sn, Hg, Pd) and possibly metal–acetylene π complexing might occur. Finally, the consequences of placing two acetylenic linkages in a case III situation (skew or criss-cross) is considered.

Results and Discussion

The results for cases I–III are presented in Charts I–III. The preparation of the starting materials is listed in Chart IV. Structures were established by analysis, molecular weight data, and spectroscopy.

The previous work in this area has shown that in case I array, type A interactions (Chart I), a metal–halogen interchange reaction on compound I with butyllithium yields not the expected IIa, but the product

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(1) (a) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951); (b) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Ruchardt, and J. D. Roberts, *ibid.*, **82**, 2646 (1960); (c) P. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, **87**, 5144 (1965); (d) M. E. Howden, Ph.D. Thesis, California Institute of Technology, 1962.

(2) (a) E. A. Hill, H. G. Richey, and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963); (b) H. G. Richey and E. A. Hill, *ibid.*, **29**, 421 (1964).

(3) P. T. Landsbury, V. A. Pattison, W. A. Clement, and J. D. Sidler, *J. Am. Chem. Soc.*, **86**, 2247 (1964).

(4) R. L. Letsinger and L. R. Nazy, *ibid.*, **81**, 3013 (1959).

(5) C. E. Castro and R. D. Stephens, *J. Org. Chem.*, **28**, 2163 (1963).

(6) R. E. Dessy and S. A. Kandil, *ibid.*, **30**, 3857 (1965).

Chart I

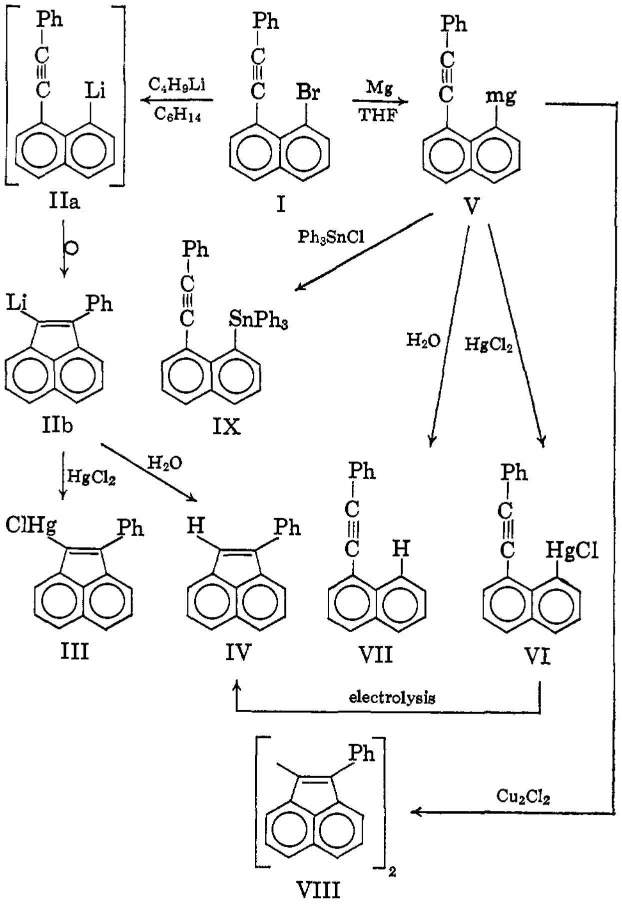


Chart II

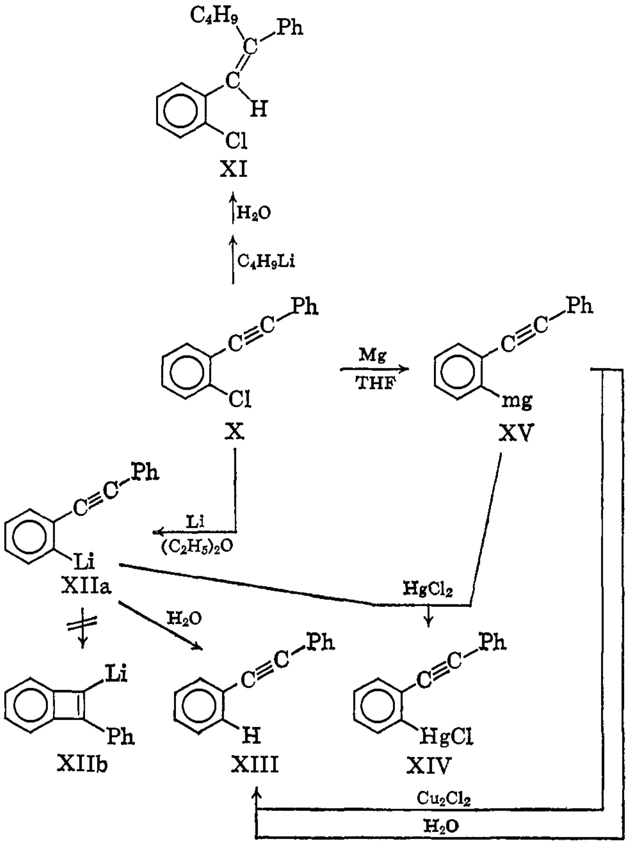
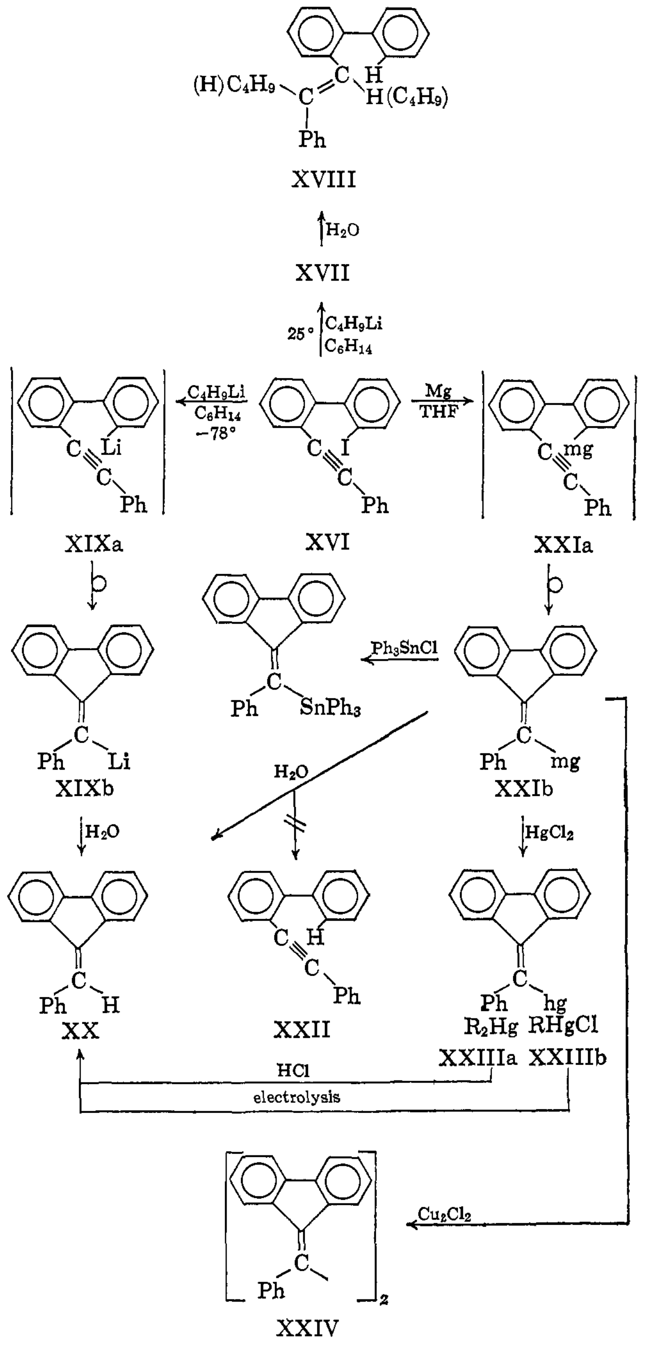


Chart III



derived from intramolecular addition to give the acenapthylenyllithium derivative IIb. This was confirmed by hydrolysis to phenylacenaphthylene (IV) and reaction with mercuric chloride to give compound III. Conversion of compound I to its Grignard reagent (V) however, did not lead to a rearranged carbon skeleton, as evidenced by hydrolysis of the phenylethynylnaphthylmagnesium bromide to phenylethynylnaphthalene (VII) and its ability to metalate mercuric chloride to give VI, the isomer of III. Two conclusions were drawn on the basis of these observations, and the qualitative assessment of the stability of the carbanions incipient in structures IIb and V by measurement of the $E_{1/2}$ values for the reduction of the subvalent species, RHg, derived from III and VI, respectively.[7] (1) organolithium reagents, with their high bond polarity,

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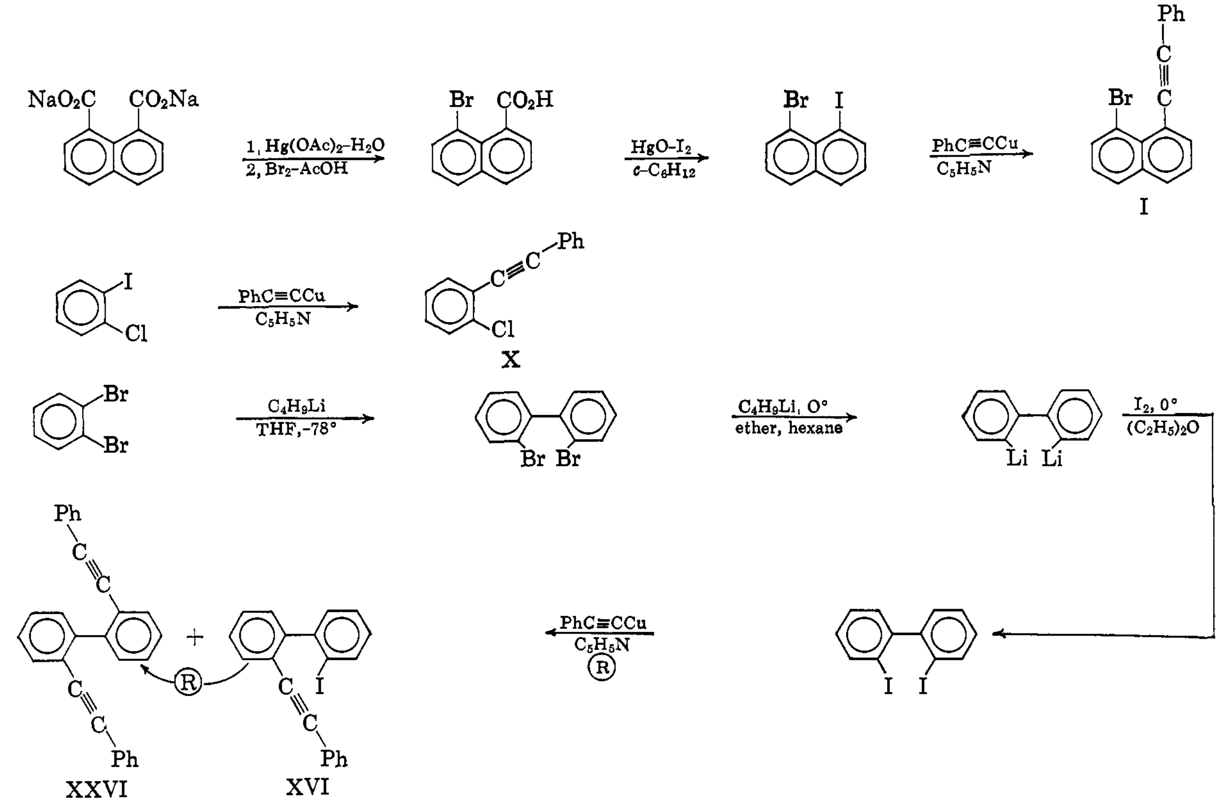
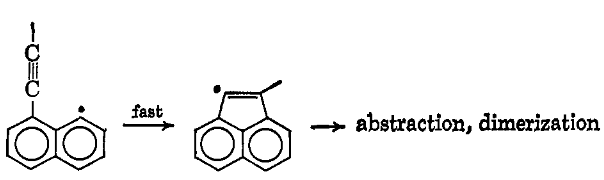
[7] The generation of carbanions from reduction of the subvalent RHg, and the correlation of $E_{1/2}$ values with carbanion stabilities, is discussed by R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen, and T. Chivers, *J. Am. Chem. Soc.*, **88**, 460 (1966).

Chart IV



are capable of effecting intramolecular addition, but organomagnesium compounds are not, and (2) the driving force for ring closure appears to be the relative stability of the incipient carbanions involved on either side of the equilibrium. To this must obviously be added the ring strain factors, elegantly studied by Roberts, Hill, and Richey as portrayed in eq 1 and 2. In type B interactions, generation of the organocopper derivative from V leads to the biacenaphthylenyl VIII as the major product, along with phenylacenaphthylene (IV) and some phenylethynylnaphthalene (VII). The fate of the organocopper reagents derived from Grignard systems involves a complex literature. The subject has been reviewed,[8] and more recently some excellent mechanistic studies have been performed.[9] It was shown that organocopper–organomagnesium complexes may form, and that in their reaction with alkyl halides in the Kharasch reaction *both* free-radical and ionic routes are involved in almost equal amounts. In the present case it is possible to consider complex electron-transfer processes yielding active carbanions, or activation of the Grignard by complexation. However, in the absence of further data, the present view considers the organocopper reagents at reflux temperatures as sources of radicals, RCu → R· + Cu. The



(3)

isolation of predominantly the ring-closed products from abstraction (IV) and coupling (VIII) suggest that the fate of the radical parallels that of the carbanion. It is of interest that controlled potential electrolysis of VI in moist dimethoxyethane, using Bu_4NClO_4 as supporting electrolyte, with three electrode geometry,[7] and at a potential sufficient to cause

$$RHgX \xrightarrow{e} X^- + RHg \xrightarrow{e} Hg + R:^-$$

leads to the ring-closed hydrocarbon IV. The carbanion ring closes before it reacts with water, indicating the closure is quite facile, with a low activation energy. The hydrolysis of organolithiums is certainly practically diffusion controlled[10]—the counterion in this case is Bu_4N^+, and the carbanion is relatively "hot." It is suggested that this route to free carbanions may be of value to those interested in carbanionoid rearrangements.[11]

Case II array (Chart II) suggests that ring closure reactions to four-membered systems by type A interactions will be difficult as are the numerous fascinating methods known to not make cyclobutadienes.[12]

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[8] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954.

[9] (a) V. D. Parker, L. H. Prette, R. M. Salinger, and C. R. Noller, *J. Am. Chem. Soc.*, **86**, 1110 (1964); (b) V. D. Parker and C. R. Noller, *ibid.*, **86**, 1112 (1964).

[10] M. Orchin, I. Wender, and R. A. Friedel, *Anal. Chem.*, **21**, 1973 (1949).

[11] A previous report[6] indicated that electrolysis gave unclosed materials. The ultraviolet evidence quoted therein is correct, but the control amplifier employed limited at 40 v, and the electrolysis proceeded by the $E_{test} - E_{ref}$ potential slowly climbing the i/E curve. The actual compound that resulted was R_2Hg, derived from 2RHg → R_2Hg + Hg. In the present case a slaved set of Kepco power supplies, boot strapped for high-input impedance, gave a cell working potential of 160/v and the amplifier was in control at all times. This is an important point to watch in this method of carbanion generation.

[12] The literature in this area is vast. The reader is referred to Cava's definitive studies: (a) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **78**, 800 (1956); (b) M. P. Cava and M. J. Mitchel, *ibid.*, **81**, 5409 (1959); (c) M. P. Cava and R. Pohlke, *J. Org. Chem.*, **27**, 1564 (1962), and to Emerson's trapping experiments: (d) G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).

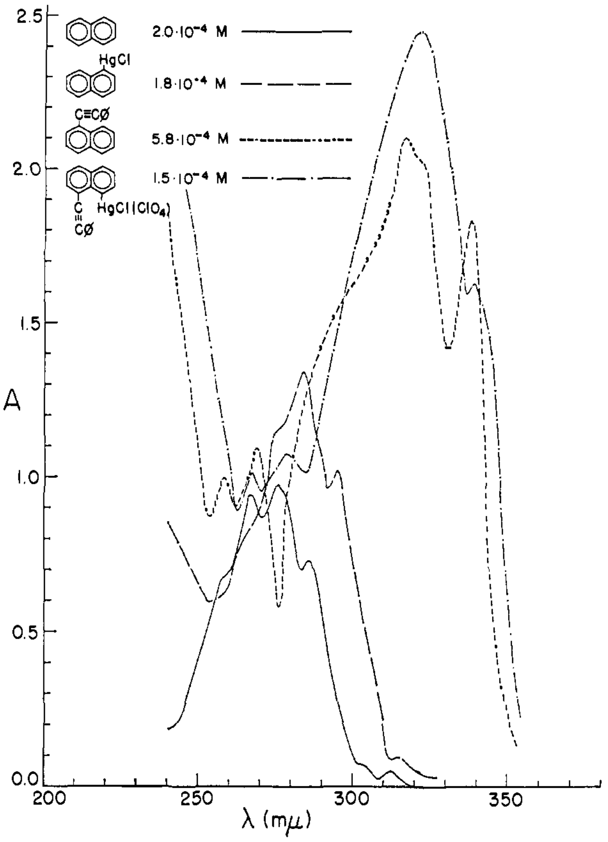

Figure 1.

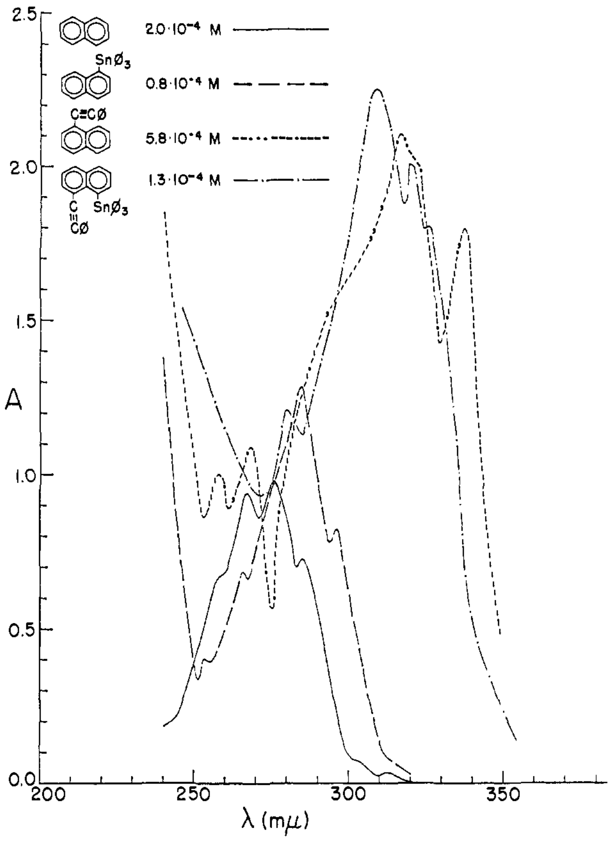

Figure 2.

o-Chlorodiphenylacetylene reacts with butyllithium at reflux temperatures to give only the product of addition across the triple bond (XI). Surprisingly no metal–halogen interchange occurred. Mulvaney[13a] has reported that *n*-butyllithium adds to and metalates diphenylacetylene concurrently. *p*-Chlorophenylacetylene gives butylphenylacetylene, perhaps *via* a benzyne intermediate.[13b] He also reports that *t*-butyllithium electron transfers into diphenylacetylene giving the radical anion, which couples to the dianion. However, the desired organolithium reagent (XIIa) can be obtained in the present case by the direct reaction shown. Hydrolysis gives the expected diphenylacetylene (XIII). No evidence for products derived from the benzocyclobutadienyllithium (XIIb) could be found. As might be expected, the strain is unfavorable to closure. The organomagnesium derivative of *o*-chlorodiphenylacetylene (XV) does not close either, as shown by its conversion to the same chloromercury derivative (XIV) as may be obtained from the lithium reagent (XIIa). Finally, type B interaction, *via* the organocopper derivative from XV, yields only diphenylacetylene *via* abstraction.

Case III array, type A interactions (Chart III) reveal some similarity to case I. Attempts at preparing the desired organolithium reagent from compound XVI, by treatment with butyllithium at room temperature led to addition/metal–halogen interchange concurrently, yielding XVIII upon hydrolysis. The nature of the polymer or its precursor was not studied. At −78° only metal–halogen interchange occurred, but the lithium reagent involved as an intermediate was not XIXa, but the ring-closed product XIXb which yielded benzylidenefluorene (XX) upon hydrolysis. No evidence for a closure to the six-membered ring derivative, 5-phenyl-6-lithiophenanthrene, could be found. *This synthesis opens up a new route to alkylidenefluorene derivatives.* Surprisingly, the organomagnesium derivative XXI of the starting halide ring closed after formation, as shown by its hydrolysis to benzylidenefluorene (XX) not phenylethynyldiphenyl (XXII). Its reactions with mercuric chloride therefore yielded a mixture of the bisorganomercury (XXIIIa) and the organomercuric chloride (XXIIIb). As expected, HCl cleavage of XXIIIa gives ring-closed hydrocarbon XX not XXII. Finally, electrolysis of the RHgCl compound, as described earlier, gives the ring-closed hydrocarbon XX, indicating that the cyclization is not an equilibrium process. Preparation of the organocopper derivative from the Grignard reagent (XXIb) leads to a dimer, probably bi(benzylidenefluorenyl) (XXIV).

The marked difference between the behavior of the organomagnesium derivatives in cases I and III arrays is most likely the result of a combination of specific acetylene distortions by metal ion (Li *vs.* Mg), and the geometrical dissimilarities in the two cases.

In all three array cases, type C interactions would be of theoretical interest. Numerous examples of metal–acetylene complexes are available. These range from the transient $(RC{\equiv}CR)_2 \cdot Hg^{2+}$ complex[14] involved in acetylene hydration, to the $(RC{\equiv}CCu)_x$ polymers,[15] and thence to the more civilized $RC{\equiv}CR \cdot$

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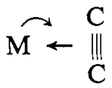
[13] (a) J. E. Mulvaney, Z. G. Gardland, and S. L. Gardland, *J. Am. Chem. Soc.*, **85**, 3898 (1963); (b) J. E. Mulvaney, personal communication.

[14] W. L. Budde and R. E. Dessy, *J. Am. Chem. Soc.*, **84**, 1172 (1962).

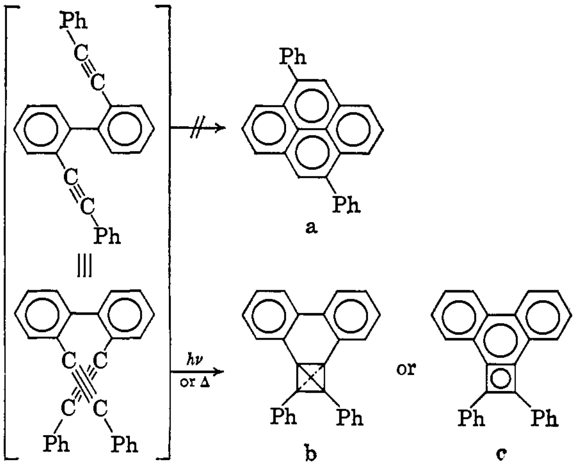
$CO_2(CO)_6$,[16] $(C_5H_5Ni)_2 \cdot RC{\equiv}CR$,[16] or $(Fe(CO)_3)_2 \cdot RC{\equiv}CR$.[16] The existence of relatively stable C_6H_5—M bonds derived from the transition series[16] (Ni, Pd, and Pt, in particular) would suggest that inclusion of these metals in arrays I, II, or III might lead to stable compounds involving



interactions. Attempts at this employing $PdCl_2$ in interaction with Grignard reagents V, or XV, failed to give any traceable products. The HgX derivatives (compounds VI and XIV) and one $(C_6H_5)_3Sn$ derivative (compound IX) were isolable in excellent yields however.

Attempts at assessing the nature and extent of type C interactions for these compounds by ultraviolet spectral observations on the HgX, $Hg^+(ClO_4^-)$, and $Sn(C_6H_5)_3$ compounds, in comparison with the proper model compounds, was made. A portion of the data appears in the earlier paper.[6] For availability to future workers, the pertinent data appear in Figures 1–3 and the Experimental Section. The present workers feel nothing would be gained by their discussion of the results.

Chart V



XXVI XXVII

In addition to metal–acetylene interactions, the present system offers an opportunity to study acetylene–acetylene interactions (Chart V). If 2-iodo-2′-phenylethynylbiphenyl (XVI, Chart IV) is treated with phenylethynylcopper in refluxing pyridine, two products are obtained. The first is 2,2′-diphenylethynylbiphenyl (XXVII, mp 118–119°, 65% yield). This latter compound was obtained in 30% yield from the former upon exposure to the sun for 1 week. Both compounds XXVI and XXVII show the expected molecular weight (354) *via* osmometry and mass spectrometric analysis (direct inlet, 105 and 150°, respectively). Only a parent peak and a peak at mass/charge ratio of 177 were observed for either compound. On the basis of mode of synthesis, analysis, and molecular weight data, compound XXVII may have three possible structures. These involve (a) a pyrene skeleton, (b) a tricyclo-[1.1.0.0^{2,4}]butane nucleus, or (c) a cyclobutadiene derivative. Structure XXVIIa may be eliminated on the basis of the ultraviolet spectrum.[17] Compound XXVII shows (95% alcohol) λ_{max} 343 mμ (ϵ 51 $\times$ 10^2), 328 (57 $\times$ 10^2), 291 (646 $\times$ 10^2), 281 (519 $\times$ 10^2), 262 (278 $\times$ 10^2), 250 (273 $\times$ 10^2), 242 (265 $\times$ 10^2). A differentiation between the two remaining structures is being attempted by Dr. Jerome Karle, using single-crystal X-ray studies.

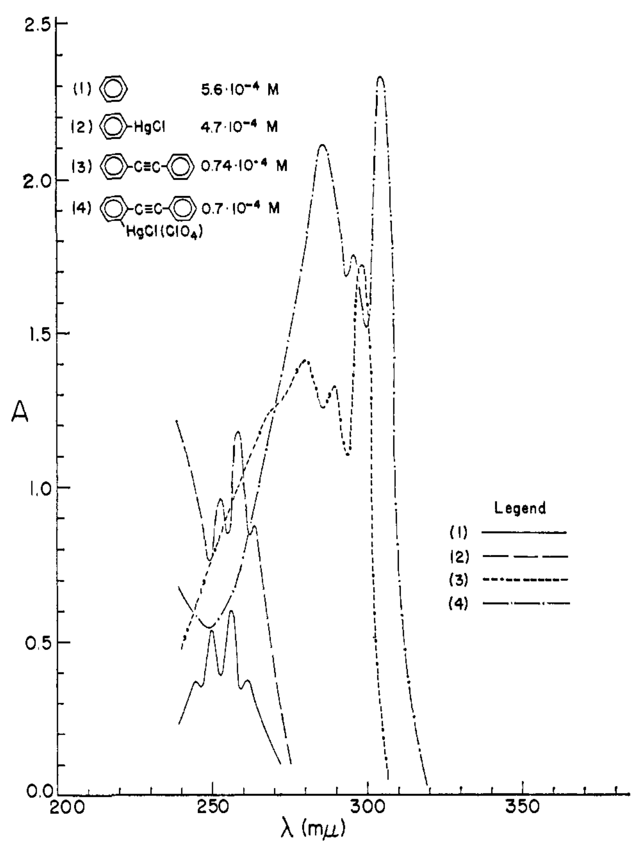


Figure 3.

Experimental Section

All compounds were analyzed correctly for C and H (Hg and Sn) by Galbraith Laboratories. Molecular weight data (Mechrolab osmometer) were within 5% of the expected value. Infrared spectra were obtained on a Perkin-Elmer Infracord; ultraviolet spectra were recorded on a Cary Model II (Applied Physics Corp.). Ozonolysis experiments were performed with the help of Mr. Fred Oehlschleger, Emery Industries. The route to starting materials is indicated in Chart IV. Refer to Charts I–III for other compounds.

Case I (Chart I). The synthesis of compounds I–VII has been previously described[6] as have their ultraviolet spectra.

Attempted Preparation of 1-Phenylethynyl-8-naphthylcopper (VIII). The Grignard reagent of 1-phenylethynyl-8-bromonaphthalene (4 g) in 50 ml of THF was prepared and after all the magnesium had reacted a suspension of CuCl in THF was added to the reagent. The mixture was refluxed for 2 hr. Cooling was followed by hydrolysis with dilute HCl. Extraction with ether, followed by evaporation, gave a brown semisolid. This was chromatographed on a packed column of neutral alumina using ligroin to give two fractions, a and b. Fraction a, after evaporation, gave 1-phenylethynylnaphthalene; b, after evaporation, gave an orange oil which proved to be 1-phenylacenaphthylene (mp 54–55°, ultraviolet spectra). Ether was then used to elute the remaining red band on the column which yielded a blood-red solid. This was recrystallized from benzene–alcohol to give a blood-red crystalline solid, mp 249–250° (0.5 g, 20% yield).

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(15) G. E. Coates in "Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1962.

(16) W. Hubel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959).

(17) R. O. C. Norman, G. A. Thompson, and W. A. Waters, *J. Chem. Soc.*, 175 (1959).

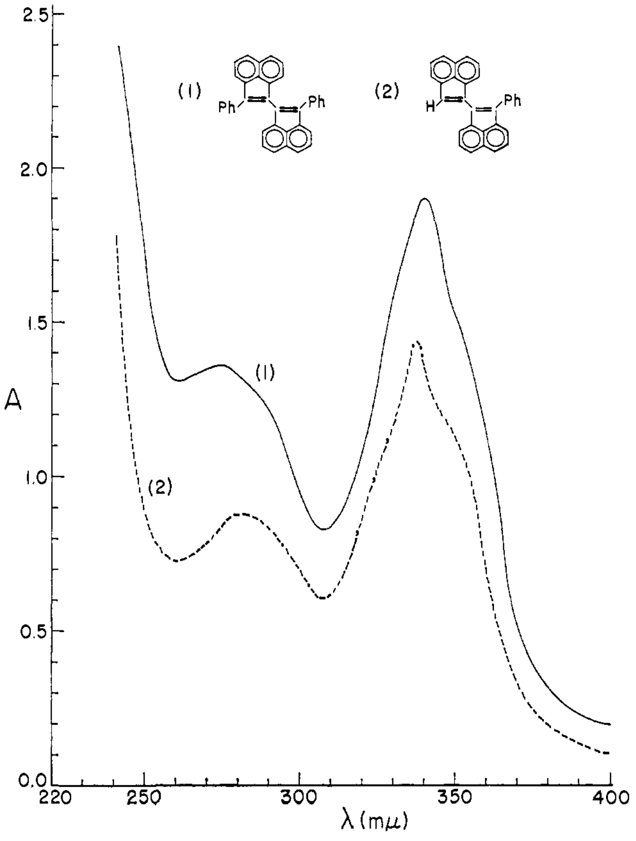

Figure 4.

Anal. Calcd for $C_{18}H_{11}$: C, 95.15; H, 4.85; mol wt, 454. Found: C, 94.88; H, 5.34; mol wt, 451.

The identity of its spectra with the model compounds[18] shown in Figure 4 confirms the structure shown; $\lambda_{\max}^{\mathrm{THF}}$ 340 mμ (ϵ 30,000), 338 (29,000), 332 (26,000).

1-Phenylethynyl-8-naphthyltriphenyltin (IX). The Grignard reagent of 1-phenylethynyl-8-bromonaphthalene (4 g) was prepared in THF. A solution of triphenyltin chloride in THF was then added and the reaction mixture was stirred at room temperature for 10 hr. Hydrolysis followed by extraction and evaporation of the ether solvent yielded a semisolid. Addition of ethanol gave a white solid. This was recrystallized from alcohol–benzene to give the white, crystalline 1-phenylethynyl-8-naphthylyltriphenyltin, mp 219–220° (2.1 g, 28% yield); $\lambda_{\max}^{\mathrm{THF}}$ 332 mμ (ϵ 15,200), 309 (16,300), 280 (8500).

Anal. Calcd for $C_{36}H_{26}Sn$: C, 74.90; H, 4.50; mol wt, 576. Found: C, 74.77; H, 4.41; mol wt, 570.

1-Naphthyltriphenyltin was prepared from the Grignard reagent of 1-bromonaphthalene and triphenyltin chloride. The procedure has been reported[19] elsewhere; $\lambda_{\max}^{\mathrm{THF}}$ 296 mμ (ϵ 6700), 285 (8500), 274 (7500).

Case II (Chart II). *o*-Chlorodiphenylacetylene (X). A solution of *o*-chloroiodobenzene (15 g) in acetic acid was thoroughly purged with nitrogen. Phenylethynylcopper[6] (10.3 g) was added and the mixture was refluxed for 5 hr. The reaction was then cooled and water was added. Extraction with ether followed by separation, drying, and evaporation of the solvent yielded a brown oil. This was distilled to give some starting material (80° at 1 mm). The product, *o*-chlorodiphenylacetylene, distilled at 140–145° (1 mm)[20] as a very pale yellow oil (7 g, 52.2% yield). The dibromide was prepared in chloroform. Evaporation of the solvent and recrystallization from benzene yielded white crystals, mp 179–181°.

Anal. Calcd for $C_{14}H_9Br_2Cl$: C, 44.9; H, 2.44: Br, 41.8. Found: C, 45.5; H, 2.41; Br, 41.27.

1-(*o*-Chlorophenyl)-2-phenylhexene (XI). To a hot solution of o-chlorodiphenylacetylene (8 g) in ether was added a solution of *n*-butyllithium in hexane (36.4 ml, 15% solution). The color became red at once and after addition was completed the reaction was refluxed for 8 hr. Cooling followed by hydrolysis and ether extraction yielded an oil after evaporation of the solvent. The oil was distilled under reduced pressure to give a pale liquid (XI), bp 156–158° (4 mm), in 80% yield.

Anal. Calcd for $C_{18}H_{19}Cl$: C, 79.85; H, 7.02. Found: C, 82.10; H, 7.22.

The nmr spectra showed a vinylic proton at τ 3.2. A sample was ozonized and hydrolysis of the ozonide yielded *o*-chlorobenzaldehyde as one of the products (identified as the 2,4-dinitrophenylhydrazone, mp 207–209°).

Diphenylacetylene (XIII) from *o*-Chlorodiphenylacetylene and Lithium. Freshly chopped lithium wire (0.17 g) was added to an ethereal solution of *o*-chlorodiphenylacetylene and the mixture was refluxed for 5 hr. The reaction was cooled and hydrolyzed with 10% HCl. Extraction with ether followed by separation, drying, and evaporation gave an oil. This was chromatographed using ligroin (bp 40–60°). After evaporation of the solvent, the resulting oil solidified readily to give white solid diphenylacetylene, mp 60–62° (3.8 g, 95% yield); $\lambda_{\max}^{\mathrm{THF}}$ 299 mμ (ϵ 23,000), 290 (17,000), 280 (22,000).

***o*-Chloromercuridiphenylacetylene (XIV) from the Organolithium.** The above reaction was carried out, a solution of mercuric chloride in THF was added, and the mixture was stirred for 2 hr. Hydrolysis and ether extraction were followed by separation, drying, and evaporation of the solvent, yielding a semisolid. This on chromatography, using benzene as eluent, yielded a white solid, *o*-chloromercuridiphenylacetylene, after evaporation, mp 192–194° (5 g, 50% yield). Analytical data appear below.

Diphenylacetylene (XIII) from *o*-Chlorodiphenylacetylene and Magnesium. A solution of *o*-chlorodiphenylacetylene (5 g) in dry THF was added dropwise to activated magnesium (0.6 g). After addition was completed the reaction was refluxed for 5 hr. Most of the magnesium had disappeared and the reaction was cooled and hydrolyzed. Extraction with ether was followed by separation, drying over anhydrous magnesium sulfate, and evaporation, yielding an oil. This was chromatographed using ligroin (bp 40–60°). After evaporation of the solvent the resulting oil solidified readily to give the white solid, diphenylacetylene, mp 60–63° (3.8 g, 95% yield).

***o*-Chloromercuridiphenylacetylene (XIV) from the Grignard Reagent.** The above reaction was carried out using 0.4 g of magnesium. After all the magnesium disappeared a solution of mercuric chloride in THF was added and the mixture was refluxed for 2 hr. The reaction was cooled and worked up in much the same manner. Evaporation of the eluted benzene solution gave a white, crystalline solid, *o*-chloromercurydiphenylacetylene, mp 192–194° (5 g, 50% yield). The analysis sample was recrystallized from ethanol–benzene mixture.

Anal. Calcd for $C_{14}H_9HgCl$: C, 40.68; H, 2.18. Found: C, 40.82; H, 2.44.

Diphenylacetylene (XIII) from the Grignard Reagent and CuCl. The above reaction was carried out and to the Grignard reagent CuCl was added and the reaction refluxed for 2 hr. Hydrolysis and work-up using chromatography with ligroin (bp 40–60°) as eluent yielded an oil after evaporation of the solvent. The oil solidified readily to give diphenylacetylene (3.4 g, 85% yield).

Case III (Chart III). 2,2′-Dibromobiphenyl was prepared from *o*-dibromobenzene and *n*-butyllithium in THF. The procedure and yields are reported elsewhere.[21]

2,2′-Diiodobiphenyl. 2,2′-Dibromobiphenyl (15 g) was dissolved in dry ether and the solution was cooled to 0°. A solution of *n*-butyllithium in hexane (61.6 ml, 15% solution) was added dropwise keeping the temperature at about 0°. The reaction started at once and the color of the solution turned greenish. After the addition was completed the reaction was stirred at room temperature for a period of 4 hr. The mixture was then cooled again to 0° and a solution of iodine (12.3 g) in dry ether was added dropwise. The color of the iodine discharged at once and at the end of the addition a faint yellow color persisted. The reaction was then allowed to stir at room temperature for 1 hr and hydrolyzed with 1% hydrochloric acid solution. Extraction, separation, drying, and evaporation of the solvent gave a very pale yellow solid. This

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(18) The authors wish to thank D. C. C. Smith for the samples necessary for this comparison: *cf.* S. O'Brien and D. C. C. Smith, *J. Am. Chem. Soc.*, 2905 (1963).

(19) E. Krause and M. Schmitz, *Ber.*, **52**, 2157 (1919).

(20) M. S. Newman and D. E. Reid, *J. Org. Chem.*, **23**, 665 (1958).

(21) H. Gilman, *ibid.*, **22**, 447 (1957).

was recrystallized from alcohol to give white needles of 2,2′-diiodobiphenyl (15 g, 76.9% yield), mp 108–109°.[22]

2-Iodo-2′-phenylethynylbiphenyl (XVI). 2,2′-Diiodobiphenyl (34 g) was dissolved in pyridine (500 ml) that was purged with nitrogen. Phenylethynylcopper (13.8 g) was added and the mixture was then refluxed for a period of 10 hr. The reaction was then cooled and water was added. Extraction with ether followed by separation, drying, and evaporation of the solvent gave a brown oil. The oil was chromatographed on neutral alumina using ligroin (40–60°) to give a yellow solution. This on evaporation gave a yellow oil that solidified readily on standing to give a white solid, 2-iodo-2′-phenylethynylbiphenyl (23.7 g, 25.2% yield). The solid was recrystallized from alcohol–ether to give a white solid, mp 70–71°; λ_{max}^{THF} 305 mμ (ε 19,000), 296 (shoulder) (17,000), 288 (21,000).

Anal. Calcd for $C_{29}H_{13}I$: C, 63.16; H, 3.42; I, 33.42. Found: C, 63.30; H, 3.35; I, 33.24.

***t*-1-(2′-Biphenylyl)-2-phenylhexene (XVIII) and/or *t*-1-Phenyl-2-(2′-biphenylyl)hexene.** Two grams of 2-iodo-2′-phenylethynylbiphenyl was dissolved in ether and the solution was cooled in an acetone–Dry Ice mixture to the lowest attainable temperature. A solution of *n*-butyllithium in *n*-hexane (10 ml of 15% solution) was then added dropwise over a period of 3 hr. After addition of *n*-butyllithium was completed the reaction was allowed to warm up rapidly to room temperature. It was then stirred for a period of 8 hr. The mixture was then hydrolyzed and extracted with benzene–ether mixture. The organic layer was separated and dried and the solvent was evaporated to yield a thick oil. This was chromatographed using ligroin (bp 40–60°) to give a pale yellow solution which on evaporation gave a solid. This was recrystallized from ethanol to give white crystals, mp 115–116° (0.4 g, 25% yield).

Anal. Calcd for $C_{24}H_{24}$: C, 92.30; H, 7.69; mol wt, 312. Found: C, 92.18; H, 7.69; mol wt, 312 (mass spectrometer, direct inlet, 95°).

Ether was then used to elute the column of remaining material, giving a yellow solution which on evaporation yielded a yellow oil which in turn solidified readily to give a whitish yellow solid. This was recrystallized from alcohol to give a yellowish white powder.

Anal. Calcd: C, 88.85; H, 7.05; mol wt, 884. This was not investigated further.

Benzylidenefluorene (XX). The above reaction was repeated. After addition of the butyllithium was completed the reaction was left at −70° for 5 hr and then allowed to warm up very slowly to 0°. The mixture was then hydrolyzed with dilute aqueous HCl and extracted with ether. Evaporation gave a bright yellow oil. This was chromatographed using ligroin (bp 40–60°) to give a yellow solution which yielded a yellow oil after evaporation. The oil solidified readily to give a yellowish white solid of benzylidenefluorene (0.9 g, 67.7% yield).

A sample was recrystallized from heptane to give yellow crystals, mp 75–76°;[23] λ_{max}^{THF} 328 mμ (broad) (ε 15,000).

Anal. Calcd for $C_2H_{14}O$: C, 94.49; H, 5.51. Found: C, 94.40; H, 5.44.

Benzylidenefluorene (XX) from the Grignard XXIb. 2-Iodo-2′-phenylethynylbiphenyl (2 g) was dissolved in THF. The solution was added dropwise to activated magnesium. The reaction started at once. After addition was completed, the mixture was stirred for 2 hr. It was then hydrolyzed with dilute, aqueous HCl and extracted with ether. Evaporation gave a dark brown oil. This was chromatographed using ligroin (bp 40–60°) to give a slightly yellow solution which yielded a yellow oil after evaporation. The oil solidified readily to give as a yellowish white solid, benzylidenefluorene (1 g, 75% yield).

Benzylidenefluorenylmercury Compounds (XXIII). The Grignard reagent of 2-iodo-2′-phenylethynylbiphenyl was prepared in THF (6 g, 30 ml). A solution of mercuric chloride in THF (10 g, 25 ml) was then added. Heat evolved and the reaction was stirred at room temperature for 10 hr. The mixture was filtered and the filtrate was concentrated; then ethanol was added. The solid which precipitated was filtered and redissolved in THF. The solution was chromatographed using THF to give the following results.

A. An orange solution yielded an orange solid. This was recrystallized from acetone to give the orange solid benzylidenefluorenylmercuric chloride, mp 260–261° (2.5 g, 23.5% yield); λ_{max}^{THF} 322 mμ (ε 13,000), 307 (11,000), 262 (32,000), 253 (3000).

Anal. Calcd for $C_{20}H_{13}HgCl$: C, 49.08; H, 2.66. Found: C, 48.42; H, 2.96.

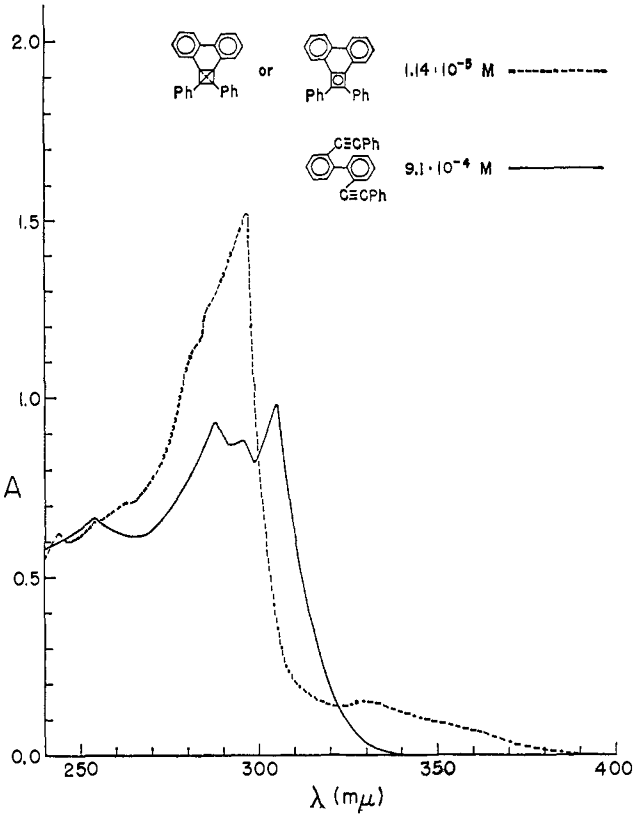

Figure 5.

B. A yellow solution on evaporation yielded a yellowish white solid. The analysis sample was recrystallized from acetone to give yellowish white lustrous leaflets of the bismercury compound, mp 306–307° (1.4 g, 12.5% yield).

Anal. Calcd for $C_{40}H_{26}Hg$: C, 67.8; H, 3.68; mol wt, 706. Found: C, 66.7; H, 3.90; mol wt, 706 (mass spectrometer, direct inlet, 140°).

Bibenzylidenefluorenyl (XXIV). The Grignard reagent of 2-iodo-2′-phenylethynylbiphenyl was prepared in THF (5 g, 25 ml). A suspension of copper(I) chloride was then added and the reaction was stirred at room temperature for 10 hr. The mixture was filtered and the filtrate was hydrolyzed with dilute HCl. Extraction with benzene–ether followed by separation, drying, and evaporation of the solvent gave a dark brown semisolid. Ethanol was then added and the resulting yellow solid was filtered. This was recrystallized from alcohol–THF to yield the yellow dibenzylidenefluorenyl, mp 303–305° (1 g, 33% yield).

Anal. Calcd for $C_{40}H_{26}$: C, 94.86; H, 5.14; mol wt, 506. Found: C, 95.08; H, 4.95; mol wt, 506 (mass spectrometer, direct inlet, 140°).

2-(2′-Phenylethynyl)biphenyltriphenyltin (XXV). The Grignard reagent of 2-phenylethynyl-2′-iodobiphenyl (8 g) was prepared in THF. A solution of triphenyltin chloride (8 g) in THF was then added and the reaction mixture was stirred for 5 hr. Water was then added and the reaction mixture was extracted with benzene–ether mixture. Separation of the organic layer was followed by drying and evaporation of the solvent to yield a bright yellow solid. This was recrystallized from acetone to yield bright yellow crystals (8 g, 63%), mp 286–289°; λ_{max}^{THF} 318 mμ (ε 14,000), 303 (16,000), 292 (16,000), 264 (50,000).

Anal. Calcd for $C_{38}H_{28}Sn$: C, 76.25; H, 5.15. Found: C, 77.6; H, 4.9.

***o*-Phenylethynylbiphenyl (XXII).** *o*-Iodobiphenyl (10 g) was dissolved in pyridine (100 ml) that was purged with nitrogen. Phenylethynylcopper (5.9 g) was added and the mixture was then refluxed for a period of 8 hr. The reaction was cooled and water was added. Extraction with ether, separation, drying, and evaporation of the solvent gave a brown oil. This was distilled to give the desired product, *o*-phenylethynylbiphenyl, a very pale yellow oil (bp 199–200° at 4.2 mm, 5 g, 56% yield); λ_{max}^{THF} 305 mμ (ε 19,000), 292 (22,000), 254 (25,000).

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[22] G. Wittig and G. Geissler, *Ann.*, **580**, 44 (1953).
[23] J. Theile and F. Henle, *ibid.*, **347**, 290 (1906).

Anal. Calcd for $C_{20}H_{14}$: C, 94.49; H, 5.51. Found: C, 94.62; H, 5.70.

o-**Chloromercuribiphenyl.** *o*-Iodobiphenyl (5 g) was dissolved in ether and added dropwise to activated magnesium (0.43 g). The reaction started at once and the mixture was refluxed for a period of 1 hr. A solution of mercuric chloride (5 g) in THF was then added and the mixture was stirred for another hour. The reaction was then hydrolyzed and extracted with ether–benzene. Separation, followed by drying and evaporation of the solvent, gave a solid. The solid was then treated with benzene and chromatographed on neutral alumina using benzene. Evaporation of the solvent gave a white, crystalline solid, bis(biphenylyl)mercury, mp 164–165°[24] (3.5 g, 77.8% yield).

Anal. Calcd for $C_{24}H_{18}Hg$: C, 56.4; H, 3.4. Found: C, 56.12; H, 3.34.

The bis compound (1.6 g) was dissolved in THF, and mercuric chloride (1 g) was added. The solution was stirred at room temperature for a period of 8 hr. Evaporation of the solvent gave another white crystalline solid, *o*-chloromercuribiphenyl, mp 166–167°.[24] The reaction is essentially quantitative; $\lambda_{\max}^{\mathrm{THF}}$ 245 mμ (ε 10,000).

o-**Biphenylyltriphenyltin.** The Grignard reagent of *o*-iodobiphenyl (4 g) was prepared in ether. This was added to triphenyltin chloride in a pressure tube filled with dry nitrogen. The mixture was left for 2 days at room temperature shaking occasionally. The reaction was then hydrolyzed and extracted with benzene–ether mixture. Separation, followed by drying and evaporation, gave an oil. Absolute ethanol was then added, and on shaking a white solid precipitated. This was recrystallized from alcohol–benzene to give a white crystalline solid, mp 95–96° (3.6 g, 50% yield); $\lambda_{\max}^{\mathrm{THF}}$ 246 mμ (ε 9000).

Anal. Calcd for $C_{30}H_{24}Sn$: C, 71.61; H, 4.77. Found: C, 71.36; H, 4.60.

2,2′-Diphenylethynylbiphenyl (XXVI) and Its Isomer (XXVII). 2-Iodo-2′-phenylethynylbiphenyl (10 g) was dissolved in pyridine (100 ml). Phenylethynylcopper (4.3 g) was added and the mixture was refluxed for 10 hr. The reaction was cooled, water was added, and the mixture was extracted with ether. Evaporation yielded a brown, thick oil. This was chromatographed using ether–ligroin (bp 40–60°) mixtures to give two fractions.

A. A colorless solution on evaporation yielded a clear oil which solidified readily. This was recrystallized from alcohol to give white needles of 2,2′-di(phenylethynyl)biphenyl, mp 118–119° (6.2 g, 64.5% yield); $\lambda_{\max}^{\mathrm{THF}}$ 305 mμ (ε 45,000), 296 (shoulder) (44,000) 287 (49,000).

Anal. Calcd for $C_{28}H_{18}$: C, 94.91; H, 5.09; mol wt, 354. Found: C, 94.68; H, 5.06; mol wt, 354 (mass spectrometer, direct inlet, 105°).

B. A yellow solution on evaporation yielded a yellowish white solid. This was recrystallized from an alcohol–THF mixture to give yellowish white needles, mp 235–236° (0.9 g, 9.6% yield); $\lambda_{\max}^{\mathrm{THF}}$ 343 mμ (ε 5100), 328 (5700), 291 (64,600), 281 (51,900), 262 (27,800), 250 (27,300), 242 (26,500) (Figure 5).

Anal. Calcd for $C_{28}H_{18}$: C, 94.91; H, 5.09; mol wt, 354. Found: C, 95.08; H, 5.04; mol wt, 354 (mass spectrometer, direct intel, 150°).

XXVII from the Irradiation of 2,2′-Diphenylethynylbiphenyl. 2,2′-Diphenylethynylbiphenyl (1 g) was dissolved in alcohol and the solution was placed in the sun for 1 week. The colorless solution became yellow. Evaporation of the solvent precipitated a solid. This was chromatographed as above to give 0.7 g of starting material and XXVII (0.3 g, 30% yield). Both compounds obtained were identified by melting point and ultraviolet comparison with samples obtained above.

Acknowledgment. The authors wish to acknowledge the support of the Petroleum Research Fund (PRF 1086-A-3,4) in the form of a grant and S. A. K. wishes to acknowledge the United Arab Republic government for its help and encouragement in the form of a mission grant, 1960–1965. The authors also wish to acknowledge the simulating discussions in the laboratories of Professor M. S. Newman during the period 1956–1957 where R. E. D. was made aware of this possible route to tetrahedrane derivatives, and to thank R. Bonham, Bendix Corp., for the mass spectrometer studies.

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(24) C. Courtot and M. G. Bastani, *Compt. Rend.*, **203**, 197 (1936).