The Chemical Behavior of *o*-Bis(phenylethynyl)benzene toward Some Electrophilic and Nucleophilic Reagents[1]

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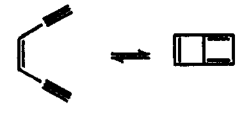
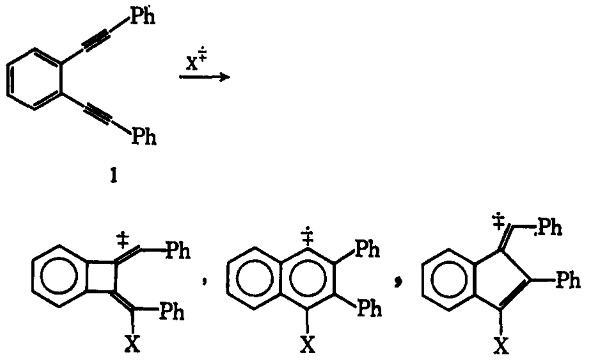
Behavior of the title compound on attack by several electrophilic, nucleophilic, radical, and reducing reagents was investigated. In all cases where reaction was observed products were derived from interaction of the two triple bonds with formation of diphenylbenzofulvenes or ring systems derived therefrom.

A possible synthetic approach to derivatives of 1,4-dehydrobenzene involves cyclization of a *cis*-1,2-diethynylethylene with 2,5 and 1,6 bridging (eq 1).



(1)

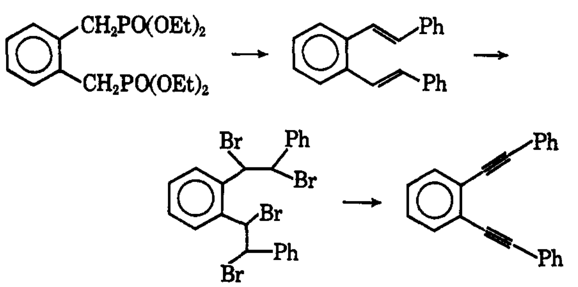
As a probe into the types of interaction possible between adjacent triple bonds of the above type, we have investigated the behavior of *o*-bis(phenylethynyl)benzene (**1**) toward a variety of reagents whose gross mechanistic behavior is fairly well understood. Müller and coworkers have recently reported preparation of some metal complexes of **1** and some observations of its behavior on irradiation.[2–5] Interaction of the triple bonds in **1** accompanying chemical reaction is interesting in that at least three ring systems can be proposed as being formed on chemical reaction of **1** (eq 2).



(2)

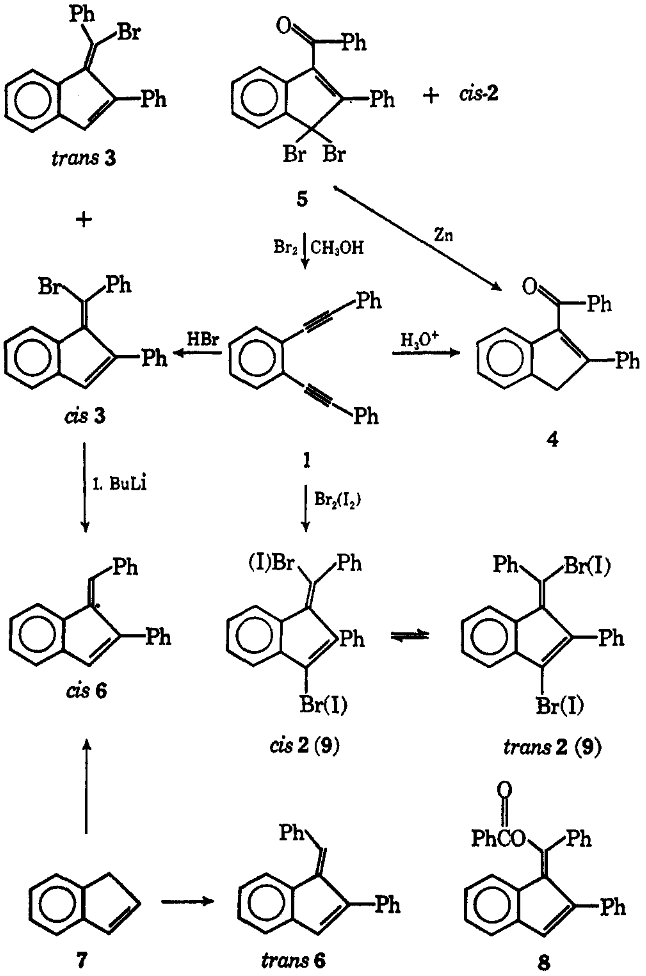
Each of these products may be derived from the attack by a reagent (X^+) orthogonal to the main π system being accompanied by folding and interaction of the two triple bonds of **1**. As detailed below we find that there is interaction between the triple bonds exclusively in the sense depicted in the third structure in eq 2: a domino folding of the triple bonds to produce derivatives of 2,8-diphenylbenzofulvene.[6]

Electrophilic Additions to 1.—The synthesis of **1** was carried out in a straightforward manner using the Wadsworth and Emmons phosphonate ester[7] route (eq 3). The reactions of **1** with electrophilic reagents are summarized in Scheme I. Identification of the



(3)

Scheme I



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[1] Part of this work was reported in a preliminary form: H. W. Whitlock, Jr., and P. E. Sandvick, *J. Amer. Chem. Soc.*, **88**, 4525 (1960).

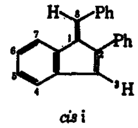
[2] E. Müller, J. Heiss, M. Sauerbier, D. Streichfuss, and R. Thomas, *Tetrahedron Lett.*, 1195 (1968).

[3] E. Müller, M. Sauerbier, and J. Heiss, *ibid.*, 2473 (1966).

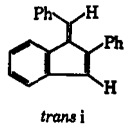
[4] E. Müller, K. Munk, P. Ziemek, and M. Sauerbier, *Naturwiss.*, **54**, 563 (1967).

[5] E. Müller, M. Sauerbier, and J. Heiss, *Trans. N.Y. Acad. Sci.*, 845 (1966).

[6] The numbering system as in i is used. The prefix *cis* indicates a cisoid arrangement of the two phenyl groups.



cis i



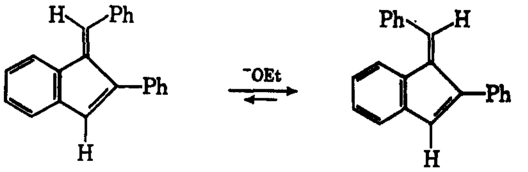
trans i

[7] W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961).

ring systems formed as benzofulvene related was based on direct comparison of three cyclized ring systems **3**, **4**, and **5** with authentic samples and comparison of the very characteristic ultraviolet (uv) spectra of the 2,8-diphenylbenzofulvenes produced with spectra of molecules known to possess this ring system. The steroeochemistry of the additions is discussed below.

Reaction of **1** with either hydrogen bromide in chloroform or hydrobromic acid in glacial acetic acid afforded in high yield the same bright yellow 1:1 adduct **3**, mp 145–147°. Its uv spectrum showed the three-peak pattern with an intense tailing of the *ca.* 340-mμ peak into the visible region characteristic of benzofulvenes.[8,9]

The structure and sterochemistry of **3** was deduced by converting it into 2,8-diphenylbenzofulvene in the following manner. Condensation of 2-phenylindene with benzaldehyde in the presence of potassium *t*-butoxide afforded both possible isomers of 2,8-diphenylbenzofulvene, the major one a yellow oil and the minor one a yellow solid, mp 129–131°. Both had the characteristic benzofulvene uv spectra[8,9] and 7.43–7.45-μ infrared (ir) bands characteristic of fulvenes.[10] The oily isomer was the more stable, being quantitatively formed on allowing the crystalline isomer to stand with potassium ethoxide in ethanol (eq 4).



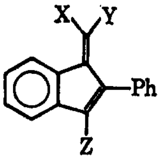
cis **6** *trans* **6** (4)

From consideration of molecular models the major isomer should be *trans*-2,8-diphenylbenzofulvene (*trans* **6**) and the minor isomer *cis* **6**. Reaction of **3** with *n*-butyllithium in tetrahydrofuran at −80° followed by quenching with water gave a mixture (predominantly *cis*) of *cis* and *trans* **6**.

The stereochemical lability of α-styryllithium compounds in good solvating solvents[11] precludes definition of the stereochemistry of **3** on the basis of its conversion into *cis* **6**. This, however, may be arrived at on an examination of the nmr spectra of **3** and other benzofulvenes prepared during the course of this work that provides a highly satisfactory method of defining their stereochemistry. In the spectrum of **3** one aromatic hydrogen appears at a characteristically low field, δ 8.17, separated from the others by *ca.* 1.2 ppm. Examination of the mother liquors from isolation of **3** revealed the presence of a material with one hydrogen appearing at a characteristically high field as a doublet ($J = 7.5$ Hz) at δ 6.11. The spectra of a number of stereoisomers of 8-halo-2,8-diphenylbenzofulvenes exhibit, for one isomer, a marked downfield shift of the signal assigned to one of the benzo ring's hydrogens and, for the other isomer, a marked upfield shift of the signal assigned to (presumably the same) the benzo ring hydrogen (Table I). Since in several cases complete spin decoupling of the four-spin system of the benzo ring could be achieved, identifying the hydrogen responsible for the anomalous signal as either H-4 or H-7, and, since there are several examples in the literature of large shifts of signals due to hydrogens in the same situation as H-7,[12–14] one may conclude that in this case the hydrogen bromide adduct isolated (**3**) is in fact *cis* **3** and the substance in the associated mother liquors is *trans* **3**. It is interesting that neither *cis* **6** nor *trans* **6** exhibited anomalous chemical shifts of H-7.

TABLE I

NMR SPECTRA



Compd	X	Y	Z	δ (H-7)	Multiplicity
cis **9**	I	Ph	I	8.80	Multiplet
trans **9**	Ph	I	I	5.85	Doublet (8 Hz)
cis **3**	Br	Ph	H	8.71	Multipet
trans **3**[a]	Ph	Br	H	6.11	Doublet (7.5 Hz)
cis **2**	Br	Ph	Br	8.65[b]	Multiplet
trans **2**	Ph	Br	Br	5.99[c]	Doublet (7.5 Hz)
trans **10**	Ph	H(D)	*n*-Bu	5.99	Doublet (7.5 Hz)
cis **6**	H	Ph	H	7.52[d]	Multiplet

[a] Not isolated. [b] Collapsed to a singlet on irradiation of the aromatic hydrogen multiplet at δ 7.2–7.5. [c] Spin decoupling of the 100-MHz spectrum (δ) gave the results: H-4, 7.26; H-5, 7.10; H-6, 6.74; H-7, 5.99 ($J_{6,7} = J_{5,6} = 7.5$ Hz; $J_{5,7} = 1$ Hz; $J_{4,6} = 1.5$ Hz; $J_{4,7} = 1$ Hz). The two phenyl rings appeared as a pair of peaks at δ 7.32 and 7.36. [d] Coupled to a 3-H multiplet at δ 7.08. H-*x* (δ 7.60) and H-*z* (δ 6.80) were doublets ($J_{XZ} = 1.2$ Hz) verified by spin decoupling.

It seems clear from both the nmr and reduction of **3** that it is in fact an 8-bromo- and not a 3-bromo-2,8-diphenylbenzofulvene. Considerable attention was de-

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(8) T. S. Cantrell and J. L. Kice, *J. Org. Chem.*, **25**, 447 (1960).

(9) N. Campbell, P. S. Davidson, and H. G. Heller, *J. Chem. Soc.*, 993 (1963).

(10) J. C. Wood, R. M. Elofson, and D. M. Saunders, *Anal. Chem.*, **30**, 1339 (1958).

(11) D. V. Curtin, J. A. Kampmeier, and M. L. Farmer, *J. Amer. Chem. Soc.*, **87**, 874 (1965).

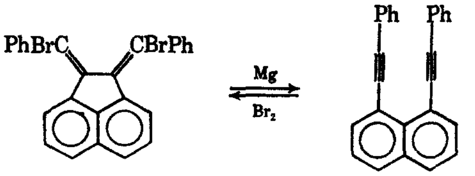
(12) H. G. Heller, D. Auld, and K. Salisbury, *J. Chem. Soc.*, *C*, 682 (1967).

(13) F. Bell and J. Spanswick, *ibid.*, 1887 (1966).

(14) G. Jones and W. J. Rae, *Tetrahedron*, **22**, 3021 (1966).

voted to achieving radical addition of hydrogen bromide to 1 but in all cases 3 was isolated.[15]

Reaction of 1 with bromine smoothly afforded two bright yellow dibromides: a major (*cis* 2) and minor isomer (*trans* 2). Both have the characteristic uv spectra of benzofulvenes and both exhibit a 7.43-μ band in their ir spectra. The kinetic *cis/trans* ratio is 3.9:1. The two isomers could be separately equilibrated on standing with bromine in chloroform to form the same equilibrium mixture, a 1.2:1 *cis/trans* mixture. Assignment of stereochemistry rests on their nmr spectra and dipole moments. The nmr spectrum of *cis* 2 exhibited H-7 as a multiplet at δ 8.65 while that of *trans* 2 had H-7 at δ 5.99. In the latter case signals of all four hydrogens at C-4–C-7 could be assigned by spin decoupling of the spectrum. *cis* 2 had a smaller dipole moment, μ = 1.27 D, than *trans*-2, μ = 1.90 D. Repeated attempts to unzip 2 by reduction were completely unsuccessful, in marked contrast to the results of Bossenbroek and Schechter[16] (eq 5) on a similar compound. Reaction of 2 with zinc, magnesium, and *n*-butyllithium under a variety of conditions wherein 1 was stable in no instances gave 1.



(5)

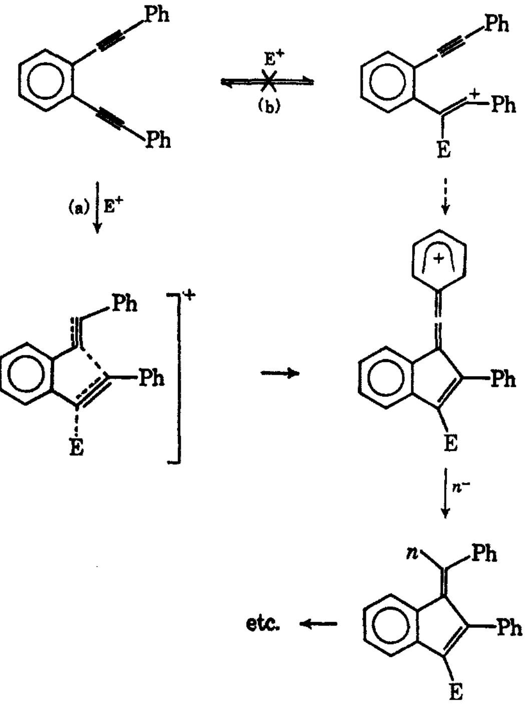
Reaction of 1 with iodine proceeded in a completely analogous manner. Two yellow orange diiodides were isolated (the *cis/trans* ratio was 3:1): the *cis* isomer exhibits a low-field multiplet at δ 8.80 in its nmr spectrum, and the *trans* isomer has a high-field doublet (J = 8 Hz) at δ 5.85. *cis–trans* isomerization of the diiodides occurred readily on recrystallization.

Reaction of 1 with bromine in methanol gave two products: dibromide *cis* 2, and a dibromo ketone (5) reducible by zinc/acetic acid to 2-phenyl-3-benzoylindene (4). Ketone 4 was synthesized, together with 8-benzoyloxy-2,8-diphenylbenzofulvene, by reaction of lithium 2-phenylindenide with benzoyl chloride. Benzoylindene 4 was also isolated on direct hydration of 1, employing either sulfuric acid in acetic acid or aqueous sulfuric acid.

Two observations suggest that electrophilic attack on 1 is accelerated in rate compared with the corresponding diphenylacetylene reactions. Comparison of the rate of the hydration reaction with the rate of the corresponding reaction of tolane (see Experimental Section) showed that 1 was quite susceptible to electrophilic attack. The ratios of the pseudo-first-order rate constants was 37 in sulfuric acid–ethanol–water at 48.9°. It seems likely from recent work that one is measuring here rate-determining proton transfer to carbon[17–20] and that the marked acceleration of electrophilic attack of 1 is due to concerted triple-bond–triple-bond interaction and *not* to rate ratios associated with partitioning of intermediate cations between proton loss and cyclization. The acceleration is marked since there must be a substantial inductive deactivating effect of the neighboring triple bond. Bromination of a 1:1 mixture of 1 and tolane resulted in the exclusive formation of 2.

The rates and stereochemical results of electrophilic addition reaction to 1 allow one to construct a mechanistic picture as shown in Scheme II.

Scheme II



The prevalence of path a over path b follows from the irreversibility of electrophilic attack and the stereochemical outcome is consistant with sp hybridization of the vinyl carbonium ion[17,21–23] coupled with least-hindered approach by the nucleophile. In Ingold's terminology[24] and as recently discussed by Fahey and Lee,[25] one may observe in suitable cases a change in mechanism of electrophilic addition to acetylenes from AdE3 for dialkylacetylenes (termolecular, concerted) to AdE2 for arylacetylenes capable of formation of resonance-stabilized carbonium ions as intermediates, although this is not a rigid dichotomy. In this light the triple bond of 1 undergoing initial attack by the electrophile suffers AdE3 electrophilic attack and the triple bond that serves as the nucleophile does so in an AdE2 manner.

Nucleophilic and Radical Addition and Reduction of 1.—Reaction of *n*-butyllithium with 1 proceeds as shown in eq 6.

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(15) Facile radical addition of hydrogen bromide to acetylenes has been reported: D.-J. Lee, Ph.D. Thesis, quoted by R. C. Fahey and D.-J. Lee, *J. Amer. Chem. Soc.*, **90**, 2124 (1968).

(16) B. Bossenbroek and H. Schechter, *ibid.* **89**, 711 (1967).

(17) D. S. Noyce and M. D. Schiavelli, *ibid.*, **90**, 1020 (1968).

(18) D. S. Noyce, M. A. Matesich, and P. E. Peterson, *ibid.*, **89**, 6225 (1967).

(19) D. S. Noyce and K. E. DeBruin, *ibid.*, **90**, 372 (1968).

(20) D. S. Noyce and M. D. Schiavelli, *ibid.*, **90**, 1023 (1968).

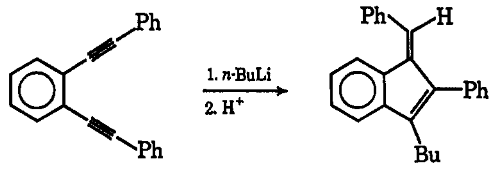
(21) R. C. Fahey and D.-J. Lee, *ibid.*, **88**, 5555 (1966).

(22) P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966).

(23) C. S. Grob and G. Gseh, *Helv. Chim. Acta*, **47**, 194 (1964).

(24) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 212, *et. seq.*

(25) R. C. Fahey and D.-J. Lee, *J. Amer. Chem. Soc.*, **90**, 2124 (1968).



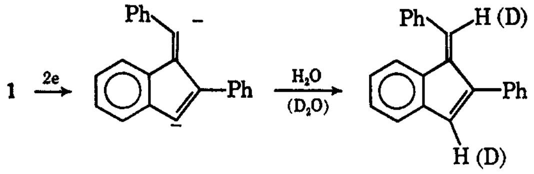
(6)

10

The structure of **10** was assigned on the basis of the characteristic uv and ir spectra of this series of fulvenes. The *trans* stereochemistry follows from the high-field position of H-7 (δ 5.99), verified by complete decoupling and identification of the resonances due to the hydrogens on the benzo ring, and initial formation of *trans*-8-lithio-2,8-diphenylbenzofulvene follows from quenching the reaction mixture with deuterium oxide that gave 8-deuterio **10**.

Addition of thiophenol to **1** proceeded sluggishly on uv irradiation to give a fulvenoid 1:1 adduct that could not be obtained analytically pure (see Experimental Section).

Reaction of **1** with lithium, or better lithium naphthalenide, in tetrahydrofuran afforded *trans*-1,8-dilithiodiphenylbenzofulvene (**11**) which on protonation afforded *trans* **6** (eq 7). Presence of *dianion* as the reaction product was verified by deuterium oxide quenching experiments. Although the stereochemical lability of α-lithiostilbenes[11] of the above type precluded a stereointerpretation of the reductive cyclization, we were interested in the question of whether or not **11** is of necessity the kinetically determined product of this reaction. One can envisage reversible reactions as shown in Scheme III coupled with the preferential formation of **11** being due to its having the negatively charged carbons at a maximum distance from one another. This is not the case, however, since addition of *o*-bis(4-deuterophenylethynyl)benzene to a solution of preformed **11**-d_0 led to no incorporation of deuterium into *trans* **6**. Inasmuch as our assumption that the dianion of **1** would undergo electron transfer to **1** competitive with its cyclization is correct the equilibrium picture in Scheme III does not exist. In this light it is interesting to note that reduction of **1** with lithium in liquid ammonia affords only the uncyclized products *o*-bis(2-phenylethyl)benzene and *o*-styrylibibenzyl; so protonation of reduced **1**, either dianion or radical anion, competes with ring closure.



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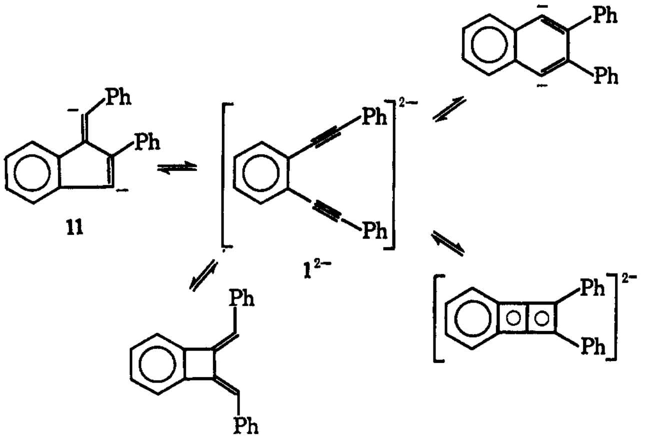
SCHEME III



The stability of dianion **11** toward opening is similar to that of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene,[26,27] since addition of *p,p'*-dideuteriodiphenylacetylene to a solution of this dianion followed by quenching led to no incorporation of deuterium into the tetraphenylbutadiene. Both dianions are apparently constituted as written.

It is interesting that the variety of reagents and reaction conditions employed here afford almost exclusively a single type of product, that arising from a domino folding of the acetylenes in **1** with concomitant formation of the 2,8-diphenylbenzofulvene ring system. While we can make a good case for electrophilic attack on **1** proceeding with concerted fulvene ring formation, the nucleophilic and radical attack do not present so clear a picture, and the reductive cyclization is clearly a two-step process.

One can generate several arguments to explain formation of the diphenylbenzofulvene ring system to the exclusion of the 2,3-diphenylnaphthalene and 1,2-bisbenzylidenebenzocyclobutene ring systems (eq 2). Formation of the naphthalene should be disfavored under all conditions owing to the considerable distance between the two carbons that must become C-2 and C-3, whereas C–C bond formation leading to the benzocyclobutadiene or fulvene could occur early in any cyclization reaction, thereby leading to a lowered activation energy for these processes. It is less clear why fulvene is favored under all conditions over benzcyclobutene, other than use of rather vague ring-strain considerations. One interesting, if speculative, possibility arises when one calculates the total π energy changes associated with the change of a 1,3,5-hexatriene π system into fulvene (by increasing the 1,5-resonance integral from 0 to 1 in 0.1 increments) or dimethylenecyclobutene (by increasing the 2,5-resonance integral).[28] While one finds that increasing $\beta_{1,5}$ from 0 to 1 leads to a smooth increase of the delocalization energy from that of hexatriene (0.988β) to that of fulvene (1.466β), increasing $\beta_{2,5}$ (dimethylenecyclobutene formation) actually leads to an initial *decrease* of the delocalization energy from 0.988 β (β_{25}, = 0) to 0.97β ($\beta_{25} \sim 0.25$) before ultimately rising to 1.208β ($\beta_{2,5}$ = 1, dimethylenecyclobutene). The repulsive interaction is small (*ca.* 1 kcal/mol) but the difference in delocalization energy for the two modes of ring closure at $\beta_{1,5}$ = 0.25 and $\beta_{2,5}$ = 0.25 corresponds to about 2.5 kcal/mol and could account for the experimental results. This type of explanation requires a concerted reaction or that all species prior to cyclization be capable of cyclizing in

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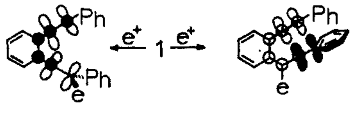
[26] L. I. Smith and H. H. Hoehn, *J. Amer. Chem. Soc.*, **63**, 1184 (1941); F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *ibid.*, **82**, 5099 (1960).

[27] V. R. Sandel and H. H. Freedman, *ibid.*, **90**, 2059 (1968).

[28] Using the simple zero-overlap HMO procedure.[29] This ignores changes in the orbitals involved in formation of the σ system of the fulvene, a process that involves orbitals orthogonal to the main π system.

[29] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961.

either direction and is not applicable to the case wherein the mode of cyclization is governed by irreversible addition of a reagent to give different uncyclized species that do not interconvert as in eq 8.



12a 12b (8)

The solid p orbitals in eq 8 are those involved in the electron-deficient π system.

Even assuming the intermediacy of **12a** and **12b** a stereoelectronic argument of the usual sort in favor of the observed mode of cyclization is available on inspection of their structures. Assuming sp hybridization of the vinyl carbonium ions it is apparent that only **12b** is set up for direct interaction between that carbon and the adjacent triple bond. Closure of **12a** must occur *via* an electrocyclic process.

Experimental Section[30]

o-**Xylylene debromide** was prepared in 50% yield by bromination of *o*-xylene according to the procedure of Stephenson.[31]

Ethyl *o*-Xylylenediphosphonate.—An adaptation of the procedure of Stilz and Pommer[32] was employed. Redistilled triethyl phosphite (139 g, 0.84 mol) was added dropwise over a 45-min period to 106 g (0.40 mol) of crude, molten *o*-xylylene debromide at 170° (oil-bath temperature) with stirring. The reaction mixture was heated at 170° for 2 hr. The water was then drained from the condenser jacket and heating was continued for 30 min with distillation of ethyl bromide formed in the reaction. The residue was heated at 100–110° (20 mm) and the yellow oily residue was used directly in the following experiment.

***o*-Distyrylbenzene.**—The general procedure of Wadsworth and Emmons[7] was used. To a stirred solution of the crude phosphonate ester from above (*ca.* 0.4 mol) and 93 g (0.88 mol) of benzaldehyde in 500 ml of dimethylformamide under nitrogen at room temperature was added 23.5 g (1 mol) of sodium hydride (43 g of a 54.7% dispersion in mineral oil) portionwise over 2 hr. When addition was complete, stirring was continued for 1 hr and then 75 ml of 95% ethanol was slowly added. The brown mixture was poured into 1.5 l. of water and the resulting mixture was refrigerated overnight and then filtered to afford 111 g of crude product. This was dissolved in 200 ml of benzene–chloroform (1:1) and the resulting solution was passed through a column of 800 g of alumina. The column was washed with benzene–chloroform (4:1) and the eluate was evaporated at reduced pressure and the residue was recrystallized from hexane–benzene to give 64.7 g of *o*-distyrylbenzene as yellow-white needles, mp 116–121° (lit.[33] mp 117.5–120°); second crop, 12.8 g, mp 113–119° (69% yield based on *o*-xylylenedibromide).

***o*-Bis(1,2-dibromo-2-phenylethyl)benzene.**—Addition of 2 equiv of bromine to a solution of *o*-distyrylbenzene in chloroform gave, on evaporation of the reaction mixture and trituration of the residue with hexane, 421 g (61%) of the tetrabromide, mp 175–183° dec. A sample was recrystallized three times from hexane–benzene to afford the analytical sample, mp 176–203° dec.

Anal. Calcd for $C_{22}H_{18}Br_4$: C, 43.89; H, 3.01; Br, 53.10. Found: C, 43.87; H, 3.00; Br, 53.19.

***o*-Bis(phenylethynyl)benzene** (1).—To a stirred solution of potassium hydroxide (12.0 g) in 200 ml of triethylene glycol (technical) at 160° was added 24.1 g (0.040 mol) of the above tetrabromide. Heating was continued at 160° for 5 min and then the brown-black reaction mixture was allowed to cool to room temperature and poured into 150 ml of saturated aqueous sodium chloride solution which was then extracted with three 50-ml portions of ether. The combined ether extracts were washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and evaporated to give 11.0 g of brown oil. The oil was adsorbed on a column of 150 g of Woelm alumina. Elution with hexane (1 l.) and hexane–ethyl acetate (49:1, 0.5 l.) gave 10.3 g (93%) of **1** as an oil which crystallized on standing.

The diacetylene was freed of stilbenelike impurities ($\lambda_{\max}^{CCl_4}$ 10.3 μ) by allowing 10.3 g of it to stir with a solution of 0.5 g of potassium permanganate in 75 ml of acetone for 2 hr at 5°. Working up and recrystallizing the product from methanol afforded 9.2 g of *o*-bis(phenylethynyl)benzene, mp 49.5–51.5°.

Anal. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 94.92; H, 4.97.

The picrate of *o*-bis(phenylethynyl)benzene was precipitated on addition of the acetylene to a saturated solution of picric acid in 95% ethanol. The analytical sample was prepared by recrystallization from 95% ethanol as orange needles, mp 96–97°.

Anal. Calcd for $C_{28}H_{17}N_3O_7$: C, 66.27; H, 3.38; N, 8.28. Found: C, 66.39; H, 3.49; N, 8.14.

Bromination of *o*-Bis(phenylethynyl)benzene.—To a stirred solution of 556 mg (2.0 mmol) of **1** in 10 ml of chloroform at 5° was added, over 5 min, 6.0 ml of a stock solution of bromine in chloroform (350 mg of bromine; 5.90 g of bromine/100 ml of solution). The reaction mixture was allowed to stand at 5° for 2 hr, washed with sodium thiosulfate solution, dried, and evaporated to afford 911 mg of an orange crystalline residue. The nmr of the residue exhibited peaks at δ 5.99 and 8.65 in the ratio 1:4.1. The residue was recrystallized from chloroform–ethanol to afford 675 mg (77% yield) of *cis* **2**: mp 139–141°; $\lambda_{\max}^{EtOH}$ 247 mμ (ϵ 22,200), 277 (19,200), 340 (11,600); δ (CCl_4) 8.65 (1 H, multiplet), collapsed to a singlet on irradiation at 7.27.

Anal. Calcd for $C_{22}H_{14}Br_2$: C, 60.30; H, 3.23; Br, 36.48. Found: C, 60.12; H, 3.19; Br, 36.45.

Recrystallization of the mother liquors of above from hexane afforded 53 mg (6% yield) of *trans* **2** as yellow needles: mp 116–118°; $\lambda_{\max}^{EtOH}$ 248 mμ (ϵ 17,800), 274 (18,400), 338 (10,200); δ (CCl_4) 5.99 (1 H, doublet, J = 7.5 Hz) assignable to H-7.

Anal. Calcd for $C_{22}H_{14}Br_2$: C, 60.30; H, 3.23; Br, 36.48. Found: C, 60.13; H, 3.44; Br, 36.23.

Broth *cis* and *trans* **2** showed the expected triplet at *m/e* 436, 438, and 440 in the ratio 1:2:1 in their mass spectra. The base peak was at *m/e* 278 (P − 2Br).

Bromination of **1** with 0.75 equiv of bromine gave a 1:3.9 mixture of *trans* and *cis* **2** (nmr). When a pure sample of *cis* **2** was allowed to stand in chloroform solution for 14 days in the presence of bromine, there was produced a 1.2:1 (by nmr) mixture of *cis* and *trans* **2**. The same ratio was arrived at starting from pure *trans* **2**.

The dipole moments of the two isomers were measured at 20° in carbon tetrachloride solution, using a type DM01 dipolemeter (Kohl Scientific Instrument Corp., El Cajon, Calif.). Least-squares treatment of the data gave μ = 1.27 D. for *cis* **2** and μ = 1.90 D. for *trans* **2**.

Iodination of *o*-Bis(phenylethynyl)benzene.—A mixture of 556 mg (2.0 mmol) of *o*-bis(phenylethynyl)benzene and 560 mg (2.2 mmol) of iodine in 3 ml of chloroform was allowed to stand at room temperature for 14 hr. A solution of 3.0 g of sodium thiosulfate in 50 ml of water was then added and the resulting aqueous mixture was extracted with three 25-ml portions of carbon tetrachloride. The combined orange extracts were filtered through a bed of anhydrous sodium sulfate and solvent was evaporated at reduced pressure to give 1.09 g of yellow crystalline residue. Recrystallization of the residue from methylene chloride–95% ethanol gave 563 mg (53% yield) of *cis* diiodide as yellow needles: mp 139–142°; $\lambda_{\max}^{EtOH}$ 247 mμ (ϵ 2.2 × 10^4), 288 (1.4 × 10^4), 348 (1.1 × 10^4); δ (CCl_4) 6.60–7.16 (10 H, multiplet with a sharp peak at 6.81), 7.16–7.55 (3 H, multiplet), 8.80 (1 H, multiplet). The analytical sample was prepared by recrystallization from methylene chloride–ethanol as yellow needles, mp 141–143°.

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(30) Melting points were determined on a calibrated hot stage. Nmr were determined on a Varian A-60 spectrometer and mass spectra were determined on a CEC-103C instrument with a heated glass inlet system. The process "work-up" entails partitioning between water and ether, washing the ether solution, drying over anhydrous sodium sulfate, and evaporating.

(31) E. F. M. Stephenson, "Organic Syntheses," Coll Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 984.

(32) W. Stilz and H. Pommer, German Patent 1,108,219 (1962); *Chem. Abstr.*, **57**, P732*f* (1962).

(33) C. E. Griffin, K. R. Martin, and B. E. Douglass, *J. Org. Chem.*, **27**, 1630 (1962).

Anal. Calcd for $C_{22}H_{14}I_2$: C, 49.65; H, 2.65; I, 47.70. Found: C, 49.80; H, 2.53; I, 47.64.

The filtrate remaining after recrystallization of *cis* 9 from the reaction mixture was evaporated under reduced pressure to give a red-orange oil, fractional crystallization of which from hexane afforded 74 mg (7%) of the *trans* diiodide (*trans* 9) as yellow crystals, mp 125–133°. Recrystallization of this from hexane afforded an analytical sample: mp 131–132°; $\lambda_{max}^{Et_2O}$ 248 mμ (sh, ε 20,000), 289 (14,400), 297 (sh, 14,000), 339 (sh, 10,800), 348 (11,700); δ (CCl_4) 5.85 (1 H, doublet, J = 8 Hz), 6.55–7.05 (1 H, multiplet), 7.05–7.26 (2 H, multiplet), 7.35 (10 H, singlet).

Anal. Calcd for $C_{22}H_{14}I_2$: C, 49.65; H, 2.65; I, 47.70. Found: C, 49.82; H, 2.65; I, 47.55.

Use of a deficiency of iodine and shorter reaction times afforded a *cis/trans* ratio of 3.1:1 (nmr).

Reaction of *o*-Bis(phenylethynyl)benzene with Hydrogen Bromide in Chloroform.—Hydrogen bromide was bubbled into a solution of 200 mg (0.72 mmol) of 1 in 40 ml of chloroform for 5 min at room temperature. The resulting yellow-orange solution was purged with nitrogen for 1.25 hr to remove excess hydrogen bromide, and the solvent was evaporated at reduced pressure to give 311 mg of an orange waxy residue. Recrystallization of the residue from 95% ethanol–ethyl acetate afforded 142 mg (55%) of the hydrogen bromide adduct *cis* 3 as yellow needles, mp 145–147°. The remainder was an uncrystallizable oil. Four recrystallizations of *cis* 3 from ethanol afforded an analytical sample: mp 145–147°; λ_{max}^{EtOH} 252 mμ (sh, ε 22,000), 274 (24,000), 339 (9900); δ ($CDCl_3$) 6.7–7.5 (14 H, multiplet), 6.86 (1 H, singlet), 8.71 (1 H, multiplet). The mass spectrum gave the expected isotopic distribution of peaks at *m/e* 358 (parent peak) and 360 (P + 2). The base peak occurred at *m/e* 279 (P − Br).

Anal. Calcd for $C_{22}H_{15}Br$: C, 73.55; H, 4.21; Br, 22.24. Found: C, 73.42; H, 4.11, Br, 22.38.

Examination of the nmr spectrum of the crude reaction product from another run showed absorption at δ 6.11 (doublet, J = 7.5 Hz) assignable to the *trans* hydrogen bromide adduct *trans* 3. Integration of the spectrum corresponded to a 15% yield of this isomer.

Reaction of the *cis*-2,8-Diphenyl-8-bromobenzofulvene (*cis* 3) with *n*-Butyllithium.—To a solution of 300 mg (0.836 mmol) of *cis* 3 in 50 ml of anhydrous ether under nitrogen at 0° was added 0.90 ml (1.25 mmol) of a 1.40 *M* solution of *n*-butyllithium in hexane. A transient red color appeared that quickly changed to yellow. The solution was stirred for 1.5 hr at 0°, quenched with 10 ml of water, and worked up to afford 276 mg of an orange waxy material. This was chromatographed on a column of 10 g of silica gel, eluting with hexane–benzene (7:1), to afford 67 mg (27%) of *cis*-diphenylbenzofulvene (*cis* 6): mp 127–134° (recrystallization of *cis* 6 from hexane sharpened the melting point to 127–130°); $\lambda_{max}^{Et_2O}$ 274 mμ (ε 31,000), 345 (14,000).

Condensation of 2-Phenylindene with Benzaldehyde. Formation of *cis*- and *trans*-2,8-Diphenylbenzofulvene.—An adaptation of the procedure of Thiele and Merck[34] was employed. A solution of 384 mg (2.00 mmol) of 2-phenylindene[35] and 1.06 g (10 mmol) of freshly distilled benzaldehyde in 55 ml of dry benzene was added dropwise under nitrogen to a solution of 142 mg of potassium in 60 ml of *t*-butyl alcohol over a 30-min period at room temperature. The resulting yellow solution was stirred for 2 hr and worked up. The residue was chromatographed on silica gel to give, in order of elution, 402 mg of *trans* 6 as an orange oil, 20 mg of a mixture of *cis* and *trans* 6, and 39 mg of *cis* 6 as yellow crystals. Evaporative distillation of *trans* 6 [160° (0.06 mm)] afforded an analytical sample: $\lambda_{max}^{Et_2O}$ 265 mμ (ε 24,600), 311 (9300); δ (CCl_4) 6.7–7.7 (complex multiplet).

Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75; mol wt, 280. Found: C, 94.28; H, 5.73; mol wt, 280 (mass spectrometry).

The yellow crystals of *cis* 6 were recrystallized from chloroform–95% ethanol to give 18 mg of needles, mp 124–129°. Recrystallization from hexane afforded an analytical sample: mp 129–131°; $\lambda_{max}^{Et_2O}$ 274 mμ (ε 31,000), 345 (14,000).

Anal. Calcd for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.27; H, 5.71; mol wt, 280 (mass spectrometer).

The minor isomer, *cis* 6, from above and the product from the dehalogenation of *cis* 3 were spectrally identical (ir and uv). A mixture melting point, 127–130°, was undepressed.

Heating a solution of *cis* 6 in methanol–benzene (1:1) containing potassium methoxide for 24 hr afforded on chromatography a 94% yield of *trans* 6 identified by its ir and uv spectra. The ir spectra of *cis* and *trans* 6 are sufficiently different that ~10% of *cis* 6 could have been detected in the product of this equilibration.

The Reaction of *o*-Bis(phenylethynyl)benzene with Hydrobromic Acid in Glacial Acetic Acid.—To a solution of 300 mg (1.08 mmol) of 1 in 90 ml of glacial acetic acid was added 45 ml of 48% hydrobromic acid. The resulting solution was allowed to stand at 25° for 13 hr. The canary yellow crystals were collected by filtration, washed with water, and dried *in vacuo* to give 304 mg (78%) of *cis* 3, mp 144–147°. The filtrate was concentrated, diluted with water, and extracted with ether to afford, after recrystallization, an additional 24 mg (7% yield) of *cis* 3, mp 143–146°. Melting point and mixture melting point established identity with that product from reaction of the diacetylene with hydrogen bromide in chloroform.

Hydration of 1 in Glacial Acetic Acid.—A stirred solution of 300 mg (1.08 mmol) of *o*-bis(phenylethynyl)benzene and 0.06 ml of concentrated sulfuric acid in 25 ml of glacial acetic acid was refluxed under nitrogen for 1 hr. The yellow reaction mixture was concentrated and diluted with chloroform, and the resulting solution was washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated to give 335 mg of orange oil. The oil was chromatographed on 100 g of silica gel, eluting with benzene–hexane mixtures, to give 292 mg (91%) of yellow oily crystals. Recrystallization of these from hexane gave 152 mg of the ketone 4 as pale yellow needles, mp 91–92.5°. The analytical sample was prepared by recrystallization from hexane: mp 92.5–93.5°; $\lambda_{max}^{Et_2O}$ 249 mμ (ε 18,900), 291 (18,100); δ ($CDCl_3$) 4.03 (2 H, singlet, methylene hydrogens), 7.10–7.67 (12 H, complex multiplet), 7.94 (2 H, multiplet, hydrogens *ortho* to carbonyl). The mass spectrum gave a peak at *m/e* 296 (parent) and the base peak at *m/e* 105 ($C_6H_5CO^+$).

Anal. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.57; H, 5.59.

The Reaction of 2-Phenylindenyl Anion with Benzoyl Chloride.—To a stirred solution of 300 mg (1.56 mmol) of 2-phenylindene in 50 ml of anhydrous ether under nitrogen at 25° was added 2.4 ml (3.1 mmol) of a 1.30 *M* hexane solution of *n*-butyllithium. Stirring was continued for 1.75 hr at 25° and then benzoyl chloride (0.19 ml, 230 mg, 1.6 mmol) was added in one portion. The reaction mixture was stirred for 2 hr more, diluted with water, and worked up to give 149 mg of a partially crystalline, orange residue. Chromatography of the residue on a column of 75 g of silica gel, eluting with benzene–hexane mixtures, gave 132 mg of 2-phenylindene (44% recovery), 108 mg (31% yield) of benzoyloxydiphenylbenzofulvene (8), and 117 mg (45% yield) of 4.

Recrystallization of 4 from hexane gave an analytical sample: mp 93.5–95°; $\lambda_{max}^{CS_2}$ 6.00 μ; $\lambda_{max}^{Et_2O}$ 250 mμ (ε 19,000), 291 (18,200). Ketone 4 from above was spectrally identical with that obtained from acid-catalyzed hydration of *o*-bis(phynylethynyl)benzene. A mixture melting point of the two was not depressed.

Anal. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.37; H, 5.58.

Recrystallization of 8 from hexane gave an analytical sample: mp 175–177.5°; $\lambda_{max}^{CS_2}$ 5.73, 7.43 μ; $\lambda_{max}^{Et_2O}$ 236 mμ (ε 31,600), 273 (33,400), 336 (12,700); δ ($CDCl_3$) 6.79–7.83 (18 H, complex multiplet), 8.25 (2 H, complex multiplet, hydrogens *ortho* to carbonyl).

Anal. Calcd for $C_{29}H_{20}O_2$: C, 86.98; H, 5.03. Found: C, 87.00; H, 5.22.

The Reaction of *o*-Bis(phenylethynyl)benzene with Bromine in Methanol.—To a solution of 900 mg (3.24 mmol) of 1 in 150 ml of methanol at 25° was added 24 ml of a stock solution of bromine (4.5 mmol) in methanol (0.19 *M*). The resulting solution was allowed to stand for 1.25 hr and was then evaporated. Aqueous sodium bisulfite was added and the resulting mixture was extracted with chloroform. The combined extracts were dried over anhydrous sodium sulfate, filtered, and evaporated to give 1.32 g of an orange-brown oil. The oil was chromatographed on 100 g of silica gel, eluting with benzene–hexane (1:4 to 3:2) to afford, in order of elution, 121 mg (12%) of dibromide *cis* 2, 238 mg (26% recovery) of starting material, 23 mg of an un-

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[34] J. Thiele and K. Merck, *Ann.*, **415**, 217 (1918).

[35] W. E. Rosen, L. Dorfman, and M. R. Linfield, *J. Org. Chem.*, **29**, 1723 (1964).

identified yellow crystalline material, and 789 mg (72%) of the dibromo ketone **5** as orange, oily crystals.

Recrystallization of the dibromide *cis* **2** from ethanol afforded 81 mg, mp 138.5–140°, identified by its mixture melting point and ir spectrum.

Recrystallization of the fourth band from hexane afforded 549 mg (50% yield) of the ketone **5** as yellow crystals, mp 113–116°. An analytical sample, mp 116–117°, was prepared by repeated recrystallization from hexane: $\lambda_{\max}^{CS_2}$ 6.03 μ; $\lambda_{\max}^{Et_2O}$ 257 mμ (ϵ 29,500), 337 (sh, 3580); δ ($CDCl_3$) 7.06–7.56 (9 H, complex multiplet), 7.56–8.00 (5 H, complex multiplet).

Anal. Calcd for $C_{22}H_{14}Br_2O$: C, 58.18; 3.11; Br, 35.19. Found: C, 58.07; H, 3.05; Br, 35.38.

Dehalogenation of the Dibromo Ketone 5 with Zinc in Aqueous Acetic Acid.—The general procedure of Woodward, *et al.*,[36] was used. To a rapidly stirred solution of 300 mg (0.661 mmol) of the dibromo ketone in 60 ml of 95% aqueous acetic acid was added in one portion 886 mg (0.0133 g-atom) of zinc dust at 25°. The mixture was stirred for 20 hr and filtered. The filtrate was evaporated, diluted with water, and worked up to give 250 mg of brown oil. The oil was chromatographed on 50 g of silica gel to afford in order of elution 82 mg of an unidentified oil ($\lambda_{\max}^{CCl_4}$ 6.01 μ), 31 mg of a mixture of this oil and the ketone **4**, and 45 mg (23%) of ketone **4**. Three crystallizations of this from hexane afforded 8 mg of **4**, mp 92–93°. The ir spectrum ($\lambda_{\max}^{CS_2}$ 6.00 μ) was identical with that of authentic 3-benzoyl-2-phenylindene prepared as above and a mixture melting point (92–93°) of the two samples was undepressed.

Competitive Bromination of Diphenylacetylene and *o*-Bis(phenylethynyl)benzene.—To a solution of 1 (100 mg, 0.36 mmol) and diphenylacetylene (64 mg, 0.36 mmol) in 10 ml of chloroform was added bromine (59 mg, 0.37 mmol). The reaction mixture was washed with sodium bisulfite, evaporated, and taken up in ether. Analysis of the 340-mμ band, which was assignable solely to the diphenylbenzofulvene chromophore, showed the fulvene to be present in 83% yield.

Procedure for Kinetic Measurement of Hydration of 1 in Sulfuric Acid–Water–Ethanol.—A solution of *o*-bis(phenylethynyl)benzene (1.82×10^{-3} *M*) in 95% ethanol–98% sulfuric acid–water (1.92:1.10:1.00 volume ratio) was thermostatted at $48.91 \pm 1.02°$. Aliquots were removed periodically and brought to room temperature, and their optical density at 273 mμ was measured. Least-squares treatment of the data (Figure 1) afforded a pseudo-first-order rate constant for disappearance of starting material of $4.74 \pm 0.24 \times 10^{-5}$ sec^{-1}. Under the same conditions, following the formation of deoxybenzoin at 279 mμ, the hydration of diphenylacetylene proceeded with a pseudo-first-order rate constant of $1.28 \pm 0.06 \times 10^{-6}$ sec^{-1}.

The Reaction of *o*-Bis(phenylethynyl)benzene with *n*-butyllithium. 2,8-Diphenyl-3-benzofulvene (10).—To a solution of 500 mg (1.80 mmol) of **1** in 50 ml of anhydrous ether under nitrogen at 1° was added 5.5 ml (12.2 mmol) of a 2.24 *M* hexane solution of *n*-butyllithium. The resulting solution was stirred for 8 hr at 0°, quenched with water, and worked up to give 705 mg of yellow oil.

Chromatography of this on silica gel afforded 271 mg of *n*-butyldiphenylbenzofulvene, recrystallization of which from methanol afforded 144 mg (24% yield) of **10** as yellow needles, mp 113–115°. The analytical sample was prepared by repeated recrystallization from methanol as bright yellow needles, mp 114–115°.

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.81; H, 7.11.

The uv spectrum of **10** was typical of the series: $\lambda_{\max}^{Et_2O}$ 225 mμ (ϵ 18,900), 266 (24,800), 319 (8250), and 326 (sh, 8050). The nmr spectrum showed the presence of an *n*-butyl group *via* resonances at δ 0.5–2.3 (9 H). All four hydrogens, H-4–H-7, on the benzo ring could be unravelled by decoupling of the 100-MHz spectrum, H-7 appearing as a sharp octet at δ 5.99 (J_{ortho} = 7.5 Hz, J_{meta} = 1 Hz, J_{para} = 0.75 Hz). The *exo*-benzylidene hydrogen appeared as a sharp singlet at δ 6.70 (1 H).

When the reaction was repeated, except that deuterium oxide was used to quench the reaction mixture, the butylbenzofulvene-d_1 isolated was spectrally the same as the undeuterated except that the singlet at δ 6.70 had disappeared.

The Reaction of *o*-Bis(phenylethynyl)benzene with Benzenethiolphenylthio-2,8-diphenylbenzofulvene.—The general procedure of Oswald, *et al.*,[37] was followed. In a 1-cm quartz uv cell was placed a solution of 500 mg (1.80 mmol) of **1** in 1.60 ml of hexane. Benzenethiol (0.25 ml, 270 mg, 2.4 mmol) was added. The resulting yellow solution was irradiated for 2 hr with a Hanovia lamp (115 V, 140 W, 60 cycles) placed at a distance of 7 cm from the cell. The yellow solution was then diluted with hexane–chloroform and extracted with three 15-ml portions of 5% aqueous sodium hydroxide solution. The organic extract was dried over anhydrous sodium sulfate, filtered, and evaporated at reduced pressure to give 610 mg of yellow oil. Chromatography of the oil on 80 g of silica gel gave in order of elution 7 mg of diphenyl disulfide, 370 mg of recovered diacetylene, and 150 mg of a yellow oil. The yellow oil was evaporatively distilled [190° (0.015 mm)] to give 131 mg (72% at 26% reaction) of an orange viscous oil: $\lambda_{\max}^{Et_2O}$ 267 mμ (ϵ 31,000), 327 (15,000); δ (CCl_4) 6.7–8.0 (complex multiplet).

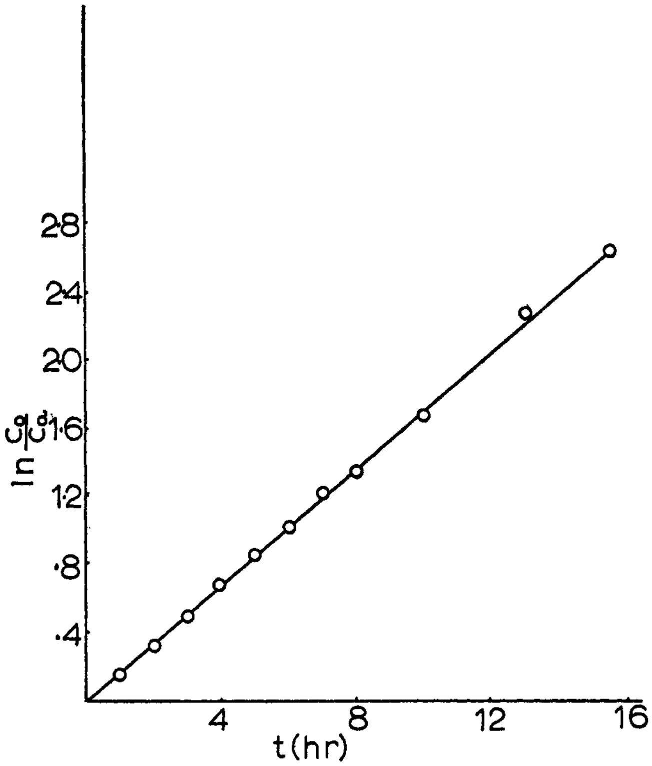

Figure 1.—Time *vs.* ln (initial concentration/concentration at time *t*) for hydration of *o*-bis(phenylethynyl)benzene in 95% ethanol–sulfuric acid at 48.9°.

Anal. Calcd for $C_{28}H_{20}S$: C, 86.55; H, 5.19; S, 8.26. Found: C, 85.91; H, 5.31; S, 8.46. Found: C, 85.99; H, 5.21; S, 8.69. Found: C, 86.01; H, 5.24.

Reaction of *o*-Bis(phenylethynyl)benzene with Lithium.—A solution of 2.00 g (7.19 mmol) of **1**, together with 0.990 g (0.143 g-atom) of lithium metal, in 150 ml of dry tetrahydrofuran was stirred under nitrogen for 3 hr at 0°. The resulting green-black solution was cooled to −80°, removed from the reaction vessel *via* a syringe, and discharged into a 300-ml mixture of water and cracked ice. The mixture was worked up to afford 2.14 g of an orange viscous oil. The oil was chromatographed on 400 g of silica gel, and afforded the following products in order of elution.

1.—A mixture of *cis*- and *trans*-diphenylbenzofulvenes totaled 1.38 g (68% yield). The *trans* isomer was eluted slightly ahead of the *cis* and was identified by comparison of its ir spectrum with that of an authentic sample. From the trailing edge there could be isolated by repeated recrystallization 20 mg of the *cis* isomer, mp 125–130°, identified by its ir spectrum. The mixture was predominantly the *trans*.

2.—A second band was 115 mg (5% yield) of a material identified as 3-benzyl-2-phenylindene: mp 60.5–62.5°; $\lambda_{\max}^{EtOH}$ 293 mμ (ϵ 22,100); δ ($CDCl_3$) 3.75 (2 H, singlet), 4.05 (2 H, singlet), 6.96–7.48 (14 H, multiplet); mass spectrum *m/e* 282 (parent), *m/e* 191 (base, P − CH_2Ph).

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[36] R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey, and R. W. Kierstead, *Tetrahedron*, **2**, 1 (1958).

[37] A. A. Oswald, K. Griesbaum, B. E. Hudson, Jr., and J. B. Bregman, *J. Amer. Chem. Soc.*, **86**, 2877 (1964).

Anal. Calcd for $C_{22}H_{18}$: C, 93.58; H, 6.42. Found: C, 93.89; H, 6.23.

3.—The last band contained three components that were separated by fractional crystallization. Each appeared to be formally dimers of diphenylbenzofulvene.

A. weighed 272 mg: mp 250–253°; $\lambda_{max}^{Et_2O}$ 218 mμ (ϵ 35,000), 286 (31,000); *m/e* 280 (base peak).

Anal. Calcd for $(C_{22}H_{16})_n$: C, 94.25; H, 5.75. Found: C, 93.89; H, 6.14; mol wt, 535, 537, 563, 582 (vapor pressure osmometer).

B. weighed 13 mg: mp 214–217°; $\lambda_{max}^{Et_2O}$ 272 mμ (ϵ 23,000); *m/e* 280 (base peak).

Anal. Calcd for $(C_{22}H_{16})_n$: C, 94.25; H, 5.75. Found: C, 93.96; H, 5.95.

C. weighed 12 mg: mp 246–252°; $\lambda_{max}^{Et_2O}$ 288 mμ (ϵ 34,000), 349 (65,000), 368 (5950), 386 (3750).

Anal. Calcd for $(C_{22}H_{16})_n$: C, 94.25; H, 5.75. Found: C, 93.96; H, 6.11.

When the above reaction was repeated, quenching with deuterium oxide rather than with water, the diphenylbenzofulvene mixture (mostly *trans*) was shown by mass spectrometry to be 0.5% d_0, 4.6% d_1, 94.9% d_2.

When the reaction between the diacetylene and lithium was followed by removing aliquots and examining their ir spectra (acetylene, 4.51 μ; fulvene, 7.45, indene, 7.19), the sequence acetylene → fulvene → indene was apparent.

Reaction of *o*-Bis(phenylethynyl)benzene with Lithium Naphthalenide.—To a solution of 1.11 g (4.00 mmol) of **1** in 30 ml of anhydrous tetrahydrofuran under nitrogen at −80° was added over 0.5 min 10.0 ml of a solution (0.92 *M*) of lithium naphthalenide in tetrahydrofuran. The resulting solution was stirred for 1 hr at −80° and then quenched by addition of 1.0 ml of methanol. The reaction mixture was evaporated, poured into water, and worked up to give 2.464 g of residue. This material was chromatographed on silica gel to afford the following products in order of elution.

1.—Naphthalene, mp 80–81°, weighed 966 mg.

2.—A mixture, 847 mg (76% yield), was *cis-* and *trans*-diphenylbenzofulvene, predominantly the latter. They were identified by comparison of their uv and ir spectra with those of authentic samples.

3.—Starting material, 34 mg (3% yield), was identified by its ir spectrum.

4.—Benzylphenylindene, 41 mg (4% yield), was identified by its infrared spectrum.

5.—An unidentified yellow oil, 74 mg, was obtained.

6.—A "dimer", 127 mg, mp 202–205°, was obtained.

Anal. Calcd for $(C_{22}H_{16})_n$: C, 94.25; H, 7.57. Found: C, 93.96; H, 5.85.

When this reaction was carried out as above, except that a fourfold excess of 1,2-dibromoethane was added to the reaction mixture which was then allowed to warm to room temperature and quenched, a 25% yield of *cis*-dibromodiphenylbenzofulvene was isolated.

Reduction of *o*-Bis(phenylethynyl)benzene in Protic Media.—These experiments can be summarized by saying that, under a variety of reaction conditions, lithium and sodium in liquid ammonia and liquid ammonia–ethanol mixtures, the diacetylene is reduced to *o*-bis(2-phenylethyl)benzene and *o*-styryldiphenylethane in varying ratios. Bis(2-phenylethyl)benzene was obtained as an oil: δ 2.82 (8 H, singlet), 7.04 (8 H, broad singlet), 7.12 (10 H, broad singlet); *m/e* 286 (parent), *m/e* 195 (base, P − CH_2Ph). It was identified by spectral comparison with a sample prepared by hydrogenation of *o*-distyrylbenzene. These properties do not agree with those quoted in the literature.[38]

Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.05; H, 7.74.

o-Styryldiphenylethane had mp 57–59°; δ 2.93 (4 H, multiplet), 6.85 (1 H, doublet, $J = 16$ Hz), 6.95–7.66 (15 H, multiplet); λ_{max}^{EtOH} 290 mμ (ϵ 18,600); $\lambda_{max}^{CCl_4}$ 10.4 μ; *m/e* 284 (parent), 193 (base peak, P − CH_2Ph).

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 93.06; H, 7.00.

In no cases were cyclized products isolated from the protic reductions.

4,4′-Dideuteriodiphenylacetylene was prepared by the following procedure: *p*-dibromobenzene[39] → *p*-deuteriobromobenzene[40] → *p*-deuterio-*p*′-dimethylaminobenzhydrol[40] → *p*-deuteriobenzaldehyde[41] → *p,p*′-dideuteriobenzoin[41] → *p,p*′-dideuteriobenzil[41] → *p,p*′-dideuteriodiphenylacetylene, mp 58–60°. The acetylene had the isotope composition 0% d_0, 1.5% d_1, and 98.5% d_2 by mass spectrometry, which adequately reflects the isotopic purity of the deuterium oxide used in the initial quenching of 4-bromophenyllithium. The nmr spectrum of deuterated tolane showed the expected pseudo-AB quartet: δ_A 7.25, δ_B 7.49 ($J_{AB} = 8$ Hz).

Entry of the 4-deuteriobenzaldehyde into the scheme for synthesis of *o*-bis(phenylethynyl)benzene afforded the *p,p*′-dideuterio species, mp 47–50°. The nmr spectrum of *o*-bis(4-deuteriophenylethynyl)benzene, 97.5% d_2, now exhibited an AB quartet: δ_A 7.25, δ_B 7.53 ($J_{AB} = 8$ Hz).

Demonstration of the Absence of Equilibrium between *o*-Bis(phenylethynyl)benzene and 2-8-Diphenyl-3,8-dilithiobenzofulvene.—To a stirred solution of 1.11 g (4.0 mmol) of **1** in 25 ml of dry tetrahydrofuran under nitrogen at −80° was added 5.0 ml of a 0.87 *M* solution of lithium naphthalenide in tetrahydrofuran (4.3 mmol of lithium naphthalenide). The resulting dark green solution was stirred at −80° for 15 min, allowed to warm to 0° (ice bath), and held at 0° for 75 min during which time the color changed to a dark brown.

A 15-ml portion of the reaction mixture was removed *via* syringe and quenched by addition to it of 1 ml of deuterium oxide. After stirring at 25° for 2 hr, this mixture was poured into water and worked up. Sequential chromatography on silica gel (to separate naphthalene from the mixture of acetylene and benzofulvene) followed by picric acid impregnated silica gel[42] to separate the latter two hydrocarbons afforded 132 mg of diphenylbenzofulvene-d_2. Its isotopic composition by mass spectrometry was 0.2% d_2, 12.2% d_1, 86.5% d_2, 0.1% d_3, and 0.9% d_4.

To the remaining reaction mixture was added at 0° a solution of 560 mg (2.0 mmol) of *o*-bis(4-deuteriophenylethynyl)benzene in 30 ml of dry tetrahydrofuran. The resulting solution was stirred at 0° for 2 hr., quenched by addition of 1 ml of methanol, and worked up to afford, after chromatography on silica gel, 1.045 g of a mixture of diacetylene and benzofulvene. A 300-mg portion of this was chromatographed on a column of picric acid impregnated silica gel[42] to afford 57 mg of benzofulvene as an orange oil. It was free of the diacetylene (ir). Its isotopic composition was 98.9% d_0, . . . d_1, 0.9% d_2, and 0.2% d_3.

When the acetylene–lithium naphthalenide reaction was allowed to proceed at −80°, for only 15 min before addition of the labeled diacetylene, the benzofulvene isolated as above had the isotopic composition 61.6% d_0 and 38.4% d_2.

Registry No.—**1,** 13203-60-6; **1** (picrate), 18887-68-8; **2** (*cis*), 14272-86-7; **2** (*trans*), 14272-87-8; **3** (*cis*), 18888-72-7; **3** (*trans*), 18888-73-8; **4,** 14272-69-6; **5,** 14272-89-0; **6** (*cis*), 14272-68-5; **6** (*trans*), 14274-88-9; **8,** 18888-76-1; **9** (*cis*), 18907-07-8; **9** (*trans*), 18907-08-9; **10** (*trans*), 18888-77-2; *o*-bis-(1,2-dibromo-2-phenylethyl)benzene, 18629-93-1; 3-benzyl-2-phenylindene, 18888-79-4; diphenylbenzofulvene (dimer), 18945-83-0; *o*-bis(2-phenylethyl)benzene, 18888-80-7; *o*-styryldiphenylethane, 18888-81-8; *p,p*′-dideuterodiphenylacetylene, 18888-82-9.

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[41] Standard laboratory procedure.

[42] J. L. Jezl, U. S. Patent 2,882,326 (1959); *Chem. Abstr.*, **55,** P22954*g* (1961). R. W. Foreman, U. S. Patent 2,941,018 (1960); *Chem. Abstr.*, **54,** P25785*d* (1960). The picric acid impregnated silica gel was prepared by addition of one part by weight of picric acid (corrected for water content) to ten parts by weight of silica gel slurried in ethyl acetate. Solvent was removed at reduced pressure and the residue was heated at 75° for 7 hr. Since picric acid was slowly eluted from the adsorbent, chromatography columns were made up with a layer of silica gel beneath the picric acid–silica gel layer. Separation of the diacetylene and the benzofulvenes was complete on this adsorbent, the latter being eluted first.