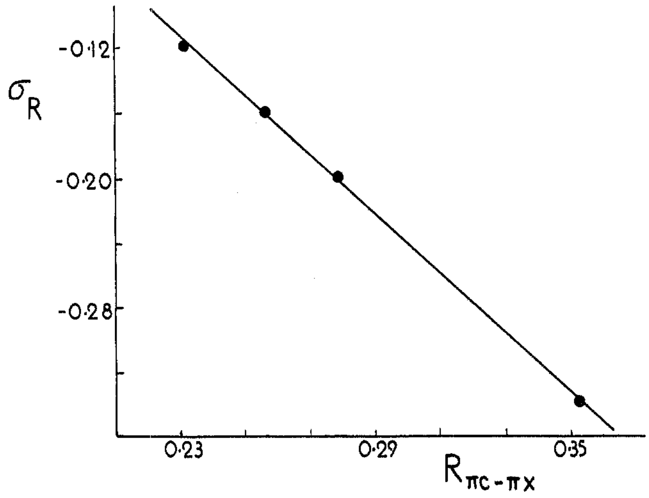

Figure 1.—Relationship between the halogen substituent constants σ_R and the repulsion integrals $R_{\pi C-\pi X}$, where X = F, Cl, Br, I. The repulsion integrals are given in atomic units (1 au = 627.2 kcal/mol).

features of some nonaromatic systems. It has already been shown that several anomalous properties of fluorine, both as a free atom and also in various inorganic and aliphatic compounds, can be explained in terms of the exceptionally strong repulsive force exerted by the fluorine atom's electrons upon any approaching electron.[22] Another interesting anomaly is the fact that the localization of the negative charge in the trihaloacetate and the trihalomethide anions appears to increase as the halogen changes from bromine to fluorine.[23,24] The least delocalization occurs with fluorine, despite its being the most electronegative. Again, this can be interpreted as the result of a very strong repulsive interaction between the fluorine electrons and the negative charge, an interaction which diminishes markedly in going on to chlorine and bromine. In columns 6–8 of Table II are presented the values of three more types of coulomb repulsion integrals: $R_{\pi C-\pi X}$, $R_{\sigma C-\pi X}$, and $R_{\sigma C-\sigma X}$.[21] These integrals represent the other possible combinations of p_π and p_σ orbitals on the carbon and the halogen atoms; they are defined analogously to $R_{\pi C-\pi X}$. In each case, the same trend is observed as before: $R_{C-F} \gg R_{C-Cl} > R_{C-Br}, > R_{C-I}$. Thus, whether any given situation of interest involves primarily one of these types of interaction or, as is more likely, two or more of them simultaneously, it is evident that a consideration of electronic repulsion interactions will help to explain many of the seemingly anomalous properties of the halogens, and of fluorine in particular.

Registry No.—F, 16984-48-8; Cl, 16887-00-6; Br, 24959-67-9; I, 20461-54-5.

Acknowledgments.—The authors wish to thank Dr. Ieva Ruks Politzer for suggesting this study, and for very helpful discussions. They also greatly appreciate the assistance of Dr. Milan Randic, Professor Frank E. Harris, and Dr. David Klint in the evaluation of the repulsion integrals.

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Synthesis and Reactivity of 2,2′-Bis(phenylethynyl)diphenylacetylene

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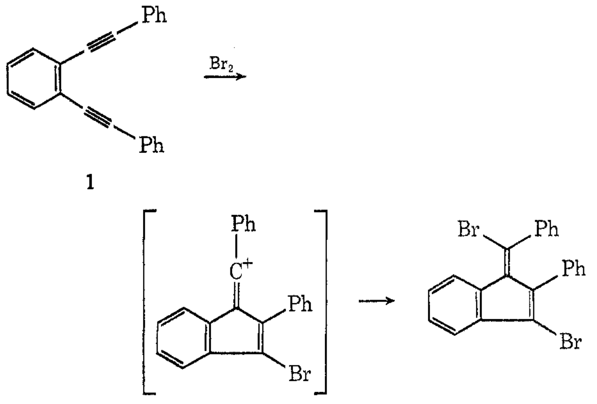
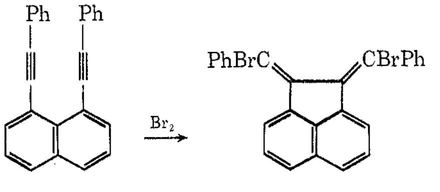
Interaction between spatially proximal acetylenic groups on chemical reaction has been demonstrated.[1–6] This occurs even if there is little angle strain to be relieved on addition of reagents (eq 1[1] and 2[5]). Evidence for the concerted nature of acetylene–acetylene interaction following attack of electrophilic reagents on **1** has been presented.[1] The type of ring system produced by addition of reagents to oligoacetylenes of this type must be at least partially dependent on the geometrical disposition of the triple bonds relative to one another. On consideration of the above results we have been prompted to synthesize the title triyne **2** to see whether it is attacked by electrophilic reagents in a manner analogous to **1**. This is observed (Scheme I).



(1)



(2)

Results

The reaction of **2** with controlled amounts of bromine affords, in addition to starting material, a mixture of di- and tetrabromides. Chromatography of the hexane-soluble portion of the reaction product afforded an oily dibromide that is assigned the gross structure **3**

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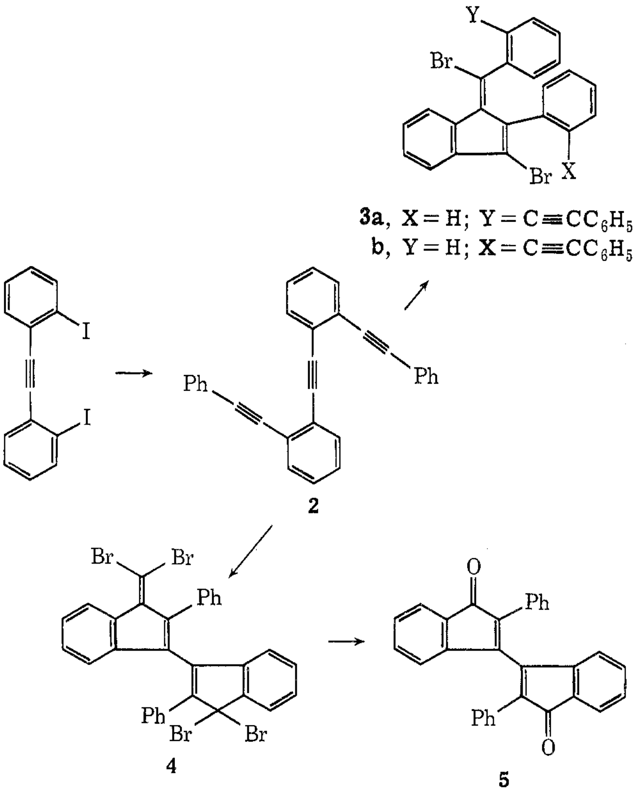
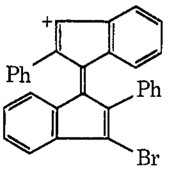
SCHEME I



on the basis of its ir and uv spectra, both characteristic of the benzofulvene chromophore. Our inability to isolate crystalline material from the oil is consistent with the presence of *cis-trans* and structural isomers (**3a** *vs.* **3b**) of **3** arising from the site of attack of bromine on **2**. The major product from bromination of **2** was a broad-melting crystalline dibromide–tetrabromide mixture. To determine the number of rings formed, this mixture was reduced with a large excess of sodium in ethanol. A low voltage mass spectrum of the product obtained indicated that hydrocarbons $C_{30}H_{24}$ and $C_{30}H_{30}$ were present in approximately equal amounts. Assuming that the aromatic rings would not be reduced under these conditions[7] the latter hydrocarbon must be derived from acyclic bromides in which *no* acetylene–acetylene bridging occurred during bromine addition. This is in marked contrast to the behavior of **1** in which bridging accompanies electrophilic attack. The $C_{30}H_{24}$ product, possessing three double-bond equivalents other than those associated with the aromatic rings, is thought to contain a double bond on the basis of the uv spectrum [$E^{1\%}_{1\,\mathrm{cm}}$ (Et_2O) 0.2 at 273 mμ] of the hydrocarbon mixture. A hydrocarbon with two rings and one double bond may arise from tetrabromide **4** (see below) or its dibromide precursor.

Reaction of **2** with a large excess of bromine afforded, in addition to the above di- and tetrabromide mixture, a crystalline and apparently homogeneous tetrabromide **4**. The isolation of 3,3′-bi(2-phenylindenone) (**5**) from the silver acetate mediated acetolysis of **4** provides confirmation of the assigned structure. Biindenone **5** was synthesized from reaction of 2-phenyl-3-bromoindenone with copper powder[8] in hot dimethylformamide.

Our results are interpretable in terms of a domino-like folding of the triple bonds in **2** similar to the behavior of **1** on electrophilic attack, at least in the initial stages of the reaction. It seems unlikely that the carbon skeleton of **4** arises in a single cyclization process as this would involve vinyl cations, *e.g.*, **6**, incapable of resonance stabilization.[9–12] Instead we feel that **4** arises as a product of secondary attack of bromine on one of the **3** species. The apparent reluctance of **2** to react with bromine relative to the reactivity of its bromination products may reflect the presence of an additional electronegative phenylethynyl substituent in **2**.



6

Experimental Section[13]

2,2′-Diiododiphenylacetylene.—To a stirred solution of 4.95 g (0.015 mol) of dibromodiphenylacetylene[14] in 50 ml of ether under nitrogen at 0° was added dropwise 21 ml (0.046 mol) of a 2.2 *M* solution of *n*-butyllithium in hexane. A stirred ethereal solution containing 14 g (0.055 mol) of iodine was then added and the dark brown solution was stirred for 30 min at 25°. After addition of 75 ml of 10% sodium bisulfite solution, the reaction mixture was worked up to afford 6.2 g of brown solid. Crystallization gave 4.4 g (69% yield) of 2,2′-diiodophenylacetylene as colorless needles: mp 106–106.5° (ethanol); $\lambda_{\max}^{\mathrm{EtOH}}$ 315 mμ (ε 16,400), 305 (13,900), 294 (20,900), 238 (25,000), 229 (26,000), with shoulders at 286 and 278 mμ; δ ($CDCl_3$, 100 MHz), 7.86 (1 H, d, J = 8 Hz), 7.59 (1 H, d, J = 7.5 Hz), 7.31 (1 H, t, J = 7.5 Hz), 7.00 (1 H, t, J = 7.5 Hz). Further splitting was observed.

Anal. Calcd for $C_{14}H_8I_2$: C, 39.10; H, 1.88. Found: C, 39.14; H, 1.91.

2,2′-Bis(phenylethynyl)diphenylacetylene (2).—A mixture of 174 mg (0.4 mmol) of 2,2′-diiododiphenylacetylene and 155 mg (0.94 mmol) of cuprous phenylacetylide[15] in 21 ml of pyridine was refluxed with stirring under nitrogen for 9 hr. The cooled reaction mixture was concentrated, diluted with water, and worked up. The product, 0.4 g, was chromatographed on Florisil to afford 93 mg (61% yield) of **2** as colorless needles: mp 108–109° (ethanol); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 4.5 μ; $\lambda_{\max}^{\mathrm{EtOH}}$ 313 mμ (ε 22,900), 292 (33,600), 265 (68,000), 250 (41,800), with shoulders at 340 and 275 mμ; δ ($CDCl_3$) 7.7–7.35 (8 H, m), 7.35–7.05 (10 H, m); R_f 0.25.

Anal. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79. Found: C, 95.23; H, 4.74.

Reaction of 2 with 1.1 Equiv of Bromine.—To a solution of 0.5 g (1.32 mmol) of **2** in 12 ml of chloroform at 0° was added, over 5 min, 0.23 g (1.45 mmol) of bromine in 25 ml of chloroform. After the mixture was stirred for 1 hr, 50 ml of 5% sodium thiosulfate solution was added. The aqueous layer was separated and extracted three times with chloroform. The combined extracts were washed with thiosulfate solution and water, dried over anhydrous sodium sulfate, and concentrated to a yellow gum. Trituration with hexane afforded 0.3 g of a yellow hexane-insoluble solid (mixture A). Repeated recrystallization of mixture A afforded yellow needles: mp 170–195° (benzene–hexane); $\lambda_{\max}^{\mathrm{MeOH}}$ 370 mμ (sh, 1900), 320 (sh, 13,300), 307 (32,500),

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295 (32,400), 282 (33,500), 273 (32,400); $\lambda_{\max}^{\mathrm{KBr}}$ 7.55 μ; R_f 0.08, 0.13, 0.21, 0.32.

Anal. Calcd for 61:39 $C_{30}H_{18}Br_2$–$C_{30}H_{18}Br_4$: C, 60.86; H, 3.07; Br, 35.97. Found: C, 60.53; H, 3.20; Br, 35.95.

The mass spectrum of mixture A (190° probe temperature) exhibited prominent peaks at 536, 538, 540 ($C_{30}H_{18}Br_2$, P), 456, 458 (P − HBr), 378 (P − 2Br), and 376 (P − 2HBr).

Preparative tlc of mixture A (11 mg) on silica gel afforded 4 mg of orange needles: mp 309–316°; $\lambda_{\max}^{\mathrm{KBr}}$ 5.97 μ; $\lambda_{\max}^{\mathrm{MeOH}}$ 430 μ (4400), 335 (15,500), 321 (15,600), 305 (21,500), 267 (51,000); *m/e* 410.

Anal. Calcd for $C_{30}H_{18}O_2$: C, 87.78; H, 4.42. Found: C, 87.81; H, 4.41.

Chromatography of the hexane-soluble fraction afforded a yellow oil in 23% yield that was a mixture of two components: R_f 0.32, 0.38; $\lambda_{\max}^{\mathrm{Et_2O}}$ 327 mμ (sh, ϵ 11,500), 275 (43,400), 244 (35,800); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 4.5, 7.41 μ; *m/e* 536, 538, 540 ($C_{30}H_{18}Br_2$, P), 457, 459 (P − Br), 378 (base, P − Br_2).

Anal. Calcd for $C_{30}H_{18}Br_2$: C, 66.94; H, 3.37; Br, 29.69. Found: C, 66.52; H, 3.58; Br, 29.84.

Triyne **2** was also isolated in 19% yield.

Reduction of Mixture A.—Sodium, 13 g, was added in small portions to a suspension of 0.3 g (0.56 mmol) of mixture A in 80 ml of refluxing ethanol. After addition of the sodium was complete, the reaction mixture was heated to reflux for 3 hr, diluted with water, and worked up to afford 239 mg of a dark green gum, $\lambda_{\max}^{\mathrm{Et_2O}}$ 273 mμ ($E^{\%1}_{1\,\mathrm{cm}}$ 0.36). Chromatography of this on silica gel afforded 130 mg (61% yield) of a pale oil, $\lambda_{\max}^{\mathrm{Et_2O}}$ 273 mμ ($E^{1\%}_{1\,\mathrm{cm}}$ 0.2). Low voltage mass spectrometry indicated the following composition: mass 384 ($C_{30}H_{24}$), 35%; 386 ($C_{30}H_{26}$), 8%; 388 ($C_{30}H_{28}$), 15%; 390 ($C_{30}H_{30}$), 32%.

Reaction of 2 with Excess Bromine.—Addition of 2.0 g (12.0 mmol) of bromine in 18 ml of chloroform to a stirred solution of 500 mg (1.32 mmol) of **2** in 10 ml of chloroform at 0° gave, after 5-min stirring and work-up, 1.0 mg of a yellow gum. Trituration of the gum with ether afforded 0.66 g of an ether-insoluble yellow solid. Three recrystallizations of this from benzene–hexane afforded 171 mg (19% yield) of a tetrabromide (**4**) as yellow needles: dec pt 200°; $\lambda_{\max}^{\mathrm{MeOH}}$ 340–355 mμ (ϵ 5600), 261 (31,400); R_f 0.32.

Anal. Calcd for $C_{30}H_{18}Br_4$: C, 51.61; H, 2.60; Br, 45.79. Found: C, 51.54; H, 2.56; Br, 45.82.

Recrystallization of the combined mother liquors from the above recrystallization afforded 400 mg of yellow needles: mp 170–185° dec; $\lambda_{\max}^{\mathrm{MeOH}}$ 307 mμ (ϵ 23,200), 274 (30,600), 370 (sh, 2200), 320 (sh, 12,600), 294 (sh, 24,800), 282 (sh, 28,200); R_f 0.1, 0.22, 0.28, 0.33.

Anal. Calcd for 60:40 $C_{30}H_{18}Br_2$–$C_{30}H_{18}Br_4$: C, 60.81; H, 3.06; Br, 36.13. Found: C, 60.35; H, 3.17; Br, 36.45.

Hydrolysis of Tetrabromide 4.—A mixture of 64 mg (0.092 mmol) of **4** and 79 mg (0.47 mmol) of silver acetate in 8 ml of acetic acid was heated under reflux for 4 hr. Water (8 ml) was added and refluxing was continued for 7 hr. The reaction mixture was filtered and the filtrate was worked up to afford 48 mg of red needles: mp 220–230° dec (benzene–hexane); $\lambda_{\max}^{\mathrm{MeOH}}$ 446–466 mμ (ϵ 3400), 261 (51,700); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.87 μ; *m/e* 410.

Anal. Calcd for $C_{30}H_{18}O_2$: C, 87.78; H, 4.42. Found: C, 87.48; H, 4.34.

3-Bromo-2-phenylindenone.—This compound was prepared by heating under reflux a mixture containing 2.2 g (0.01 mol) of 2-phenyl-1,3-indandione in chloroform and 4.3 g (0.016 mol) of phosphorus tribromide. After work-up, the crude product was chromatographed on silica gel and crystallized from hexane to give 3-bromo-2-phenylindenone, mp 73–75° (lit.[16] mp 73–74°), as orange needles in 45% yield.

3,3′-Bi(2-phenyl-1-indenone) (5).—A mixture of 197 mg (0.7 mmol) of 3-bromo-2-phenylindenone and 1 g of copper powder[8] in 6 ml of dry dimethylformamide was refluxed under nitrogen for 1 hr. An additional 1 g of copper was added and heating was continued for 3 hr. After addition of 150 ml of water, the mixture was filtered and the filtrate was worked up to afford 157 mg of a red oil. Chromatography of this on silica gel gave 19 mg (13% yield) of red solid, crystallization of which from benzene–hexane afforded 4 mg of **5**: mp 215–232° dec; $\lambda_{\max}^{\mathrm{MeOH}}$ 450–465 mμ (ϵ 3400), 261 (52,200); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.87 μ; *m/e* 410.13178 [$C_{30}H_{18}O_2$ (P) requires 410.1307], 381.12863 [$C_{29}H_{17}O$ (P − HCO) requires 381.1279], 333.09107 [$C_{24}H_{13}O_2$ (P − C_6H_5) requires 333.0916], 273.09408 [$C_{22}H_{12}$ (P − 2CO − C_6H_5) requires 267.09390]. Comparison (ir, mass spectrum) of **5** with the diketone obtained by hydrolysis of tetrabromide **4** showed them to be identical.

Registry No.—**2**, 35324-43-7; **4**, 35324-44-8; **5**, 35324-45-9; 2,2′-diiododiphenylacetylene, 35324-46-0.

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Alkene Isomerization. An Improved One-Step Synthesis of *trans*-Cyclooctene[1]

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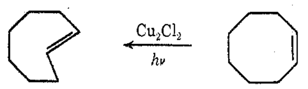
Ever since the pioneering work of Cope,[3] the unusual chemical properties of *trans*-cyclooctene (**1**) have attracted the attention of numerous chemists. In spite of the interest in this useful molecule, the published syntheses require a number of steps and/or proceed in low yield.[4] We would like to report a new procedure by which *trans*-cyclooctene (**1**) may be obtained in gram quanitities *via* one efficient light-induced step from its readily available isomer, *cis*-cyclooctene (**2**).



1 2

The isomerization of **2** was achieved by the irradiation of a stirred solution of Cu_2Cl_2 in a 2.6-fold excess of *cis*-cyclooctene at 2537 Å for 24 hr. Unisomerized **2** was removed *in vacuo* and the Cu(I) salts were successively extracted with aqueous ammonia and cyanide. Separation of **1** from **2** was accomplished by taking advantage of the former's solubility in aqueous silver nitrate.[4a] Liberation of the alkene from its silver complex afforded **1** in 19% yield (based on Cu_2Cl_2) in over 99% purity.

This photosensitized isomerization probably succeeds because the greater stability of the *trans*-cyclooctene–Cu_2Cl_2 complex shifts the equilibrium in favor of isomerization. Although other workers have employed Cu_2Cl_2 in the isomerization of alkenes which form stable complexes,[5] our work has demonstrated that prior synthesis and isolation of the Cu(I)–olefin complex is unnecessary. Thus, in addition to its convenience, our procedure allows isomerization of alkenes

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