of 2,3,4,6-tetraphenylbicyclo[3.2.1]-2-octene in which both the 6-phenyl and benzyl proton are endo and τ 6.1 (m, 0.4 H) assigned to the benzyl proton of the isomers of 2,3,4,7-tetraphenylbicyclo[3.2.1]-2-octene and the benzyl proton of the other isomers of 2,3,4,6-tetraphenylbicyclo[3.2.1]-2-octene. The mass spectrum showed m_r 412.

2,3,4-Triphenyl-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane (1), *n*-Butyllithium, and TMEDA in Hexane. To a solution of 1 (2.0 g, 0.00595 mol) and TMEDA (2.1 g, 0.0181 mol) in 125 mL of hexane was added *n*-butyllithium (0.0180 mol) in 11.2 mL of hexane. The cherry red solution was stirred for 6 h at room temperature and then terminated with excess deuterium oxide. The reaction mixture was stirred overnight, diluted with water, and extracted with ether. The combined organic layers were dried over sodium sulfate. Removal of the solvent and recrystallization from 95% ethanol afforded 2.0 g (100%) of 1. Deuterium analysis by quantitative mass spectrometry indicated 0.25 deuterium atom per molecule. The NMR spectrum ($CDCl_3$) showed no reduction in the amount of cyclopropyl hydrogen.

When the reaction was carried out under reflux for 24 h, the recovered 1 contained 0.72 deuterium atom per molecule by quantitative mass spectrometry and had a molecular weight of 337. The NMR spectrum ($CDCl_3$) showed no reduction in the cyclopropyl hydrogen.

Norbornene, *n*-Butyllithium, and TMEDA in Hexane. To a solution of norbornene (5.0 g, 0.053 mol) and TMEDA (18.6 g, 0.16 mol) in 100 mL of hexane was added *n*-butyllithium (0.157 mol) in 166 mL of hexane. The orange reaction mixture was stirred at room temperature for 6 h followed by termination with excess water. The reaction mixture was extracted with ether. The organic layers were combined and dried over sodium sulfate. Removal of the solvent gave a yellow oil, which was distilled to give 3.55 g (43.5%) of a yellow oil, bp 194–195 °C. The ultraviolet spectrum (95% ethanol) was transparent. The NMR spectrum ($CDCl_3$) showed peaks centered at τ 7.8 (b s, 1 H) assigned to the bridgehead proton at C-1 of 2-*n*-butylbicyclo[2.2.1]heptane; τ 8.1 (b s, 1 H) assigned to the other bridgehead proton; τ 8.7 (m, 18 protons) assigned to the remaining protons of 2-*n*-butylbicyclo[2.2.1]-heptane.

Anal. Calcd for $C_{11}H_{20}$: C, 86.84; H, 13.16; M_r 152. Found: C, 86.79; H, 13.23; M_r (mass spectrum) 152.

Registry No. 1, 906-84-3; 2, 906-85-4; **6a** 4-D, 78919-50-3; **6a** 4-H, 78919-51-4; **6b** 4-D, 78939-64-7; **6b** 4-H, 78919-52-5; **7a** 4-D, 78919-53-6; **7a** 4-H, 78919-54-7; **7b** 4-D, 78919-55-8; **7b** 4-H, 78919-56-9; 8 2-D, 78919-57-0; 8 2-H, 78919-58-1; 10, 61177-16-0; norbornene, 498-66-8.

Synthesis of a [16]Annuleno Analogue of Biphenylene

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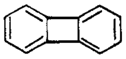
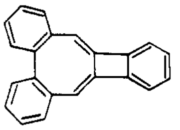
Received May 26, 1981

Analogues of biphenylene (1), in which one benzene ring is replaced by a nonbenzenoid 4*n*-π-electron system are of interest as they contain a total of (4*n* + 2)-π-electrons and so provide tests cases for the concept of peripheral delocalization which predicts enhanced stability due to aromaticity.[2] Only two such biphenylene analogues have been reported, dibenzo[*a*,*c*]benzo[3,4]cyclobuta[1,2-*f*]cyclooctene 2[2a] and the 8,9-benzo[5.2.0]nonatetraenyl anion 3,[2b] although other compounds are known in which two 4*n*-π-electron rings are fused together.[3,4] We have devised an extremely short synthesis of the [16]annulenobiphenylene derivative 7 as shown in the Scheme I. The key step involved the bis-Wittig reaction[5] between 1,2-dihydro-1,2-bis(triphenylphosphoranylidene)benzocyclobutene (4)[6] and (*E*,*Z*)-5-methylhept-2,4-dien-6-ynal (5),[7] readily prepared by homologation of (*Z*)-3-methylpent-2-en-4-ynal[8] by using the method of Cresp et al.[9]


1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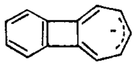
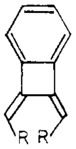
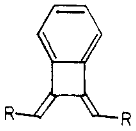
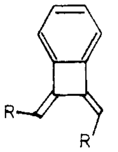

3

Reaction of the diylide 4, prepared from the corresponding phosphonium salt[6] by using butyllithium in tetrahydrofuran, with aldehyde 5 gave the adduct 6 as yellow-orange crystals in 39% yield after chromatography. Compound 6 decomposed in air at temperatures above 40 °C and underwent explosive decomposition on the mass spectrometer probe. Complete characterization was therefore not possible, and although the proton NMR and IR spectra were consistent with the assigned structure, the stereochemistry of the newly formed double bonds could not be ascertained. An examination of molecular models suggests that the (*E*,*E*)-diene **6a** is unlikely for steric reasons but that the (*Z*,*Z*)- and (*Z*,*E*)-dienes (**6b** and **6c**) do not suffer from severe steric interactions, and this is in accord with observations in the literature.[6,10]


6a (E,E-)


6b (Z,Z-)


6c (Z,E-)

R = E,Z-CH=CH-CH=C(Me)C≡CH

Dreiding molecular models indicate that only the *Z*,*E* isomer (**6c**) is capable of forming a cyclic product by oxidative coupling of the acetylenes. As the reaction product 6 appeared to be homogeneous and as it underwent cyclization (Scheme I), it was tentatively assigned structure 6c.[11] The predominance of the *Z*,*E* isomer in a bis-Wittig reaction of this type has a precedent in the literature.[10]

Intramolecular oxidative coupling was achieved by using copper(II) acetate in pyridine. The yield of this reaction varied according to the rate of addition of 6 to the reaction mixture: dropwise addition of a solution of 6 in pyridine

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[1] Present address: School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England.

[2] (a) Garratt, P. J.; Vollhardt, K. P. C.; Mitchell, R. H. *J. Chem. Soc. C* **1970**, 2137. (b) Staley, S. W.; Heinrich, F.; Orvedal, A. W. *J. Am. Chem. Soc.* **1976**, *98*, 2681.

[3] Kaplan, F. A.; Roberts, B. W. *J. Am. Chem. Soc.* **1977**, *99*, 513 and references therein.

[4] Biphenylene analogues having one benzene ring replaced by a (4*n* + 2)-π-electron system are also known, e.g.: McCulloch, R. K.; Wege, D. *Tetrahedron Lett.* **1976**, 3213. Sato, M.; Ebine, S.; Tsunetsugu, J. *Ibid.* 1977, 855 and references therein.

[5] For a review see: Vollhardt, K. P. C. *Synthesis* **1975**, 765.

[6] Blomquist, A. T.; Hruby, V. J. *J. Am. Chem. Soc.* **1967**, *89*, 4996.

[7] Darby, N.; Yamamoto, K.; Sondheimer, F. *J. Am. Chem. Soc.* **1974**, *96*, 248.

[8] Heilbron, I. M.; Jones, E. R. H.; Julia, M. *J. Chem. Soc.* **1949**, 1430.

[9] Cresp, T. M.; Sargent, M. V.; Vogel, P. *J. Chem. Soc., Perkin Trans. 1* **1974**, 37.

[10] Garratt, P. J.; Holmes, A. B.; Sondheimer, F.; Vollhardt, K. P. C. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2253.

[11] An alternative explanation is that a major product of the bis-Wittig reaction is the *Z*,*Z* isomer **6b** but that equilibration to the *Z*,*E* isomer **6c** occurs under the reaction conditions employed for the oxidative cyclization. Equilibrations of this type have been observed in similar compounds (see ref 6).

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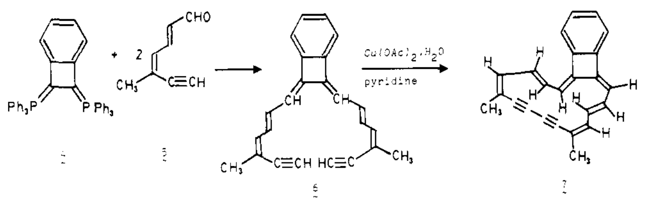
Scheme I



over 20 min gave annulene 7 in an isolated yield of less than 20% whereas a 51% yield was obtained when the addition was carried out over a period of 21.5 h.

The assignment of structure 7 to the cyclization product follows from the molecular model studies discussed earlier and was confirmed by proton NMR spectroscopy. The three inner olefinic protons resonate at low field (δ 10.00–9.20) whereas the five outer olefinic protons resonate at relatively high field (δ 6.40–5.52). These values are consistent with the magnetically induced paramagnetic ring current associated with [16]annulenes,[12] and as the phenyl protons resonate at similar chemical shifts in 6 and 7, it appears that the two ring systems in 7 are independent and that peripheral delocalization does not occur.[13]

Experimental Section

Melting points were determined on a Kofler hot-stage apparatus. Infrared (IR) spectra were recorded on a Unicam SP200 spectrophotometer in chloroform solution. Proton magnetic resonance spectra were recorded on a Varian T-60 or Varian HA-100 spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Mass spectra were determined with an AEI MS-9 or MS-12 spectrometer. Merck alumina (neutral, activity III) was used for column chromatography.

Bis-Wittig Reaction. 1,2-Dihydro-1,2-bis(triphenylphosphonio)benzocyclobutene dibromide[6] (1.34 g, 1.70 mmol) was suspended in dry THF (100 mL) and stirred at 0 °C under nitrogen. *n*-Butyllithium (1.97 M, 1.73 mL, 3.4 mmol) was added in one portion, and the mixture was stirred at 0 °C for 1 h to complete the formation of 1,2-dihydro-1,2-bis(triphenylphosphoranylidene)benzocyclobutene (4). (*E,Z*)-6-Methylhepta-2,4-dien-6-ynal (5; 0.4 g, 3.33 mmol) in THF (10 mL) was then added dropwise over 30 min to the red solution of the diylide, and the mixture was stirred at 0 °C for 1 h and then boiled under reflux for 2 h. After cooling, the reaction mixture was poured into water (100 mL) and extracted with three portions of ether (100 mL each). The organic extracts were combined and dried ($MgSO_4$), and the solvent was then removed under reduced pressure. The resulting oil was chromatographed on alumina, elution with ether–hexane (1:19) giving the *diacetylene* 6 (200 mg, 38%) as yellow-orange crystals from ether–hexane: IR ν_{max} 3300, 2100, 980 cm^{-1}; NMR δ 7.38–7.10 (4 H, m, aromatic), 7.00–6.16 (8 H, m, olefinic), 3.38 (2 H, s, 2C≡CH), 2.00 (6 H, s, 2Me).

Coupling Reaction. A solution of the diacetylene 6 (100 mg, 0.36 mmol) in pyridine (25 mL) was added dropwise over 21.5 h with a syringe pump to a rapidly stirred solution of copper(II) acetate monohydrate (3 g, 15.0 mmol) in pyridine (100 mL) at 50–60 °C under nitrogen. The reaction mixture was then stirred for another hour at 50 °C, cooled, poured into ice-cold 5% hydrochloric acid, and extracted with three portions of ether (50 mL each). The organic extracts were combined, washed with water, and dried ($MgSO_4$), and the solvent was then removed under reduced pressure. The resulting oil was purified by chromatography on alumina. Elution with ether–hexane (1:19) gave the *conjugated tricyclic product* 7 (51 mg, 51%) as purple needles (decomposing at 150 °C) from ether–hexane: IR ν_{max}(soln) 2200, 980 cm^{-1}; δ NMR 10.00–9.20 (3 H, m, olefinic), 7.22 (4 H, s, aromatic), 6.40–5.52 (5 H, m, olefinic), 1.68 (3 H, s, Me), 1.62 (3 H, s, Me): mass spectrum calcd for $C_{24}H_{18}$ *m/e* 306.1409, found *m/e* 306.1411.

Registry No. 4, 1820-39-9; 5, 55304-70-6; 6, 78871-08-6; 7, 78871-09-7; 1,2-dihydro-1,2-bis(triphenylphosphonio)benzocyclobutene dibromide, 78871-10-0.

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[12] Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811. Calder, I. C.; Gaoni, Y.; Garratt, P. J.; Sondheimer, F. *J. Am. Chem. Soc.* **1968**, *90*, 4954.

[13] Reprints of this paper will not be available.

A Caveat on the Use of Linear Free Energy Correlations with σ or σ^+ To Distinguish Transition-State Types. A Useful Graphic for the Selection of Substituents for a Linear Free Energy Study

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Received June 2, 1981

For nearly 50 years, the use of linear free energy relationships (LFER's) had dominated mechanistic organic chemistry[1] to the point that LFER's have become "fundamental" to the science.[2] The addition in 1958 of Brown's σ^+ substituent constants for electrophilic reactions[1c] "extended the validity range of the Hammet equation and allowed one to draw conclusions about conjugation in the transition state".[3] Thus, a data set which correlates with σ^+ but not with σ is thought to possess an electron-deficient site in the transition state which is in conjugation with an electron-donating substituent. In this paper we (a) demonstrate the importance of substituent selection in order to make a valid judgement regarding transition states and (b) present a graphic model to facilitate appropriate substituent selection.

We began to notice some time ago that certain data presented in the literature correlated with both σ and σ^+ to a reasonable degree.[4] An example from the recent literature[5] will suffice as an example: The rates of HCl-catalyzed *E–Z* isomerization of substituted *O*-methylbenzohydroximoyl chlorides were correlated in an LFER plot against σ, with $\rho = -0.65$ and $r = 0.993$ (the substrates utilized were *p*-OMe, *p*-Cl, H, *m*-Cl, and *p*-NO_2).[6] Against σ^+, the same five substituents afford $\rho = -0.47$ and $r = 0.980$. Thus an excellent[4] correlation is achieved with σ

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[1] (a) L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 96 (1937); (b) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953); (c) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958); (d) L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1, 35 (1963); (e) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963; (f) S. Ehrenson, *Prog. Phys. Org. Chem.*, **2**, 195 (1964); (g) C. D. Ritchie and W. F. Sager, *ibid.*, **2**, 323 (1964); (h) P. R. Wells, "Linear Free Energy Relationships", Academic Press, New York, 1968; (i) J. Shorter, *Q. Rev., Chem. Soc.*, **24**, 433 (1970); (j) N. B. Chapman and J. Shorter, Eds., "Advances in Linear Free Energy Relationships", Plenum, London, 1972; (k) K. F. Johnson, "The Hammett Equation", Cambridge University Press, New York, 1973; (l) M. Charton, *Prog. Phys. Org. Chem.*, **10**, 81 (1973); (m) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *ibid.*, **10**, 1 (1973); (n) J. Hine, "Structural Effects on Equilibria in Organic Chemistry", Wiley, New York, 1975; (o) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc., Jpn.*, **48**, 3356 (1975); (p) R. D. Topsom, *Prog. Phys. Org. Chem.*, **12**, 1 (1976); (p) S. H. Unger and C. Hansch, *ibid*, **12**, 91 (1976); (q) L. S. Levitt and H. F. Widing, *ibid.*, **12**, 119 (1976).

[2] T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", 2nd ed., Harper and Row, New York, 1981, pp 130–144.

[3] O. Exner, in ref 1j., p 33.

[4] Jaffe[1b] suggested the following terminology for describing the degree of correlation as measured by the correlation coefficient: $r > 0.99$, excellent; $r > 0.95$, satisfactory; $r > 0.90$, fair.

[5] J. E. Johnson, N. M. Silk, E. A. Nalley, and M. Arfan, *J. Org. Chem.*, **46**, 546 (1981).

[6] All values of r and ρ mentioned in this paper were calculated by using the σ and σ^+ values listed in ref 1c,d.