XL-200 superconducting spectrometer, and the chemical shifts are expressed in parts per million downfield from Me_4Si. Mass spectral analyses were done on a Hewlett-Packard GC/MS Data System, Model 5982-A. GC analyses were performed with an Antek Instrument Model 300 with a flame-ionization detector.

Tri-*p*-tolylsulfonium bromide was prepared from di-*p*-tolyl sulfoxide and *p*-tolylmagnesium bromide essentially according to a literature procedure[2] and was recrystallized from $CHCl_3$/acetone: mp 289–290 °C (lit.[2] mp 285–286 °C); ^1H NMR ($CDCl_3$) δ 2.314 (s, 9 H, methyl), 7.40 (d, 6 H, meta H's), 7.53 (d, 6 H, ortho H's).

Triphenylsulfonium bromide was prepared from diphenyl sulfoxide and phenylmagnesium bromide according to a literature procedure[2] and was recrystallized from Et_2O/EtOH: mp 247–248 °C (lit.[8] mp 241–244 °C); ^1H NMR ($CDCl_3$) δ 7.6 (br); ^{13}C NMR ($CDCl_3$) δ 123.916 (C-1), 130.698 (ortho), 131.074 (meta), 134.079 (para).

Exchange Experiments. A typical run is as follows. To sodium isopropoxide prepared by dissolving Na metal (17.3 mg, 0.75 mmol) in 2-propanol-d_1 (2 mL) was added triphenylsulfonium bromide (258 mg, 0.75 mmol) in 2-propanol-d_1 (2 mL). The mixture was stirred for 50 h at 65 °C under Ar atmosphere and was poured into ice water. The products were obtained by extracting the aqueous solution with Et_2O, washing with H_2O, drying (Na_2SO_4), and evaporation. The unreacted sulfonium salt was then recovered by extracting the aqueous solution with CH_2Cl_2. After GC and GC/MS analysis, the products were separated by preparative TLC on silica gel for characterization.

Di-*p*-tolyl Sulfide. The authentic sample was prepared by reducing di-*p*-tolyl sulfoxide with phosphorus pentasulfide in CH_2Cl_2 according to a literature procedure:[9] mp 57–58 °C (lit.[9] mp 53–55 °C); ^1H NMR ($CDCl_3$) δ 2.31 (s, 6 H), 7.09 (d, 4 H, meta H's), 7.23 (d, 4 H, ortho H's); mass spectrum, *m/e* 214 (M^+), 199, 184, 181, 165, 91.

***p*-Tolyl isopropyl ether**: ^1H NMR ($CDCl_3$) δ 1.1 (d, 6 H), 2.2 (s, 3 H), 4.0 (m, 1 H), 7.2 (d, 2 H), 7.8 (d, 2 H); mass spectrum, *m/e* 150 (M^+), 108.

Phenyl isopropyl ether: ^1H NMR ($CDCl_3$) δ 1.1 (d, 6 H), 4.0 (m, 1 H), 7.4 (br, 5 H); mass spectrum, *m/e* 136 (M^+), 94.

Acknowledgement is made to the Robert A. Welch Foundation (A-752) and the National Institutes of Health for the financial support of this work.

Registry No. Tri(*p*-tolyl)sulfonium bromide, 3744-11-4; triphenylsulfonium bromide, 3353-89-7.

(8) Knapczyk, J. W.; McEwen, W. E. *J. Am. Chem. Soc.* **1969**, *91*, 145.
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Reaction of Organolithium Compounds with a Triphenylcyclopropyl Derivative. The Matter of Cyclopropyl Anion Ring Opening

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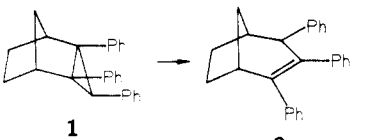
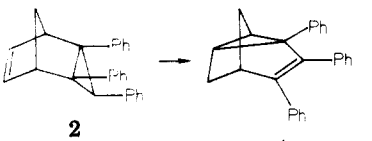
It has previously been shown that tricyclic compounds **1** and **2** react with potassium *tert*-butoxide in dimethyl sulfoxide to produce the ring opened products **3** and **4**.[1] Although these results were originally interpreted as a symmetry forbidden disrotatory opening of a cyclopropyl anion, there is now good reason to believe that this reaction proceeds by electron transfer followed by anion-radical opening of the phenyl-substituted cyclopropane.[2] Among



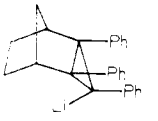
1 **3**



2 **4**

arguments presented by the Newcomb group favoring the anion radical were the facts that **1** does not undergo ring opening with KO-*t*-Bu–crown ether or lithium diisopropylamide in tetrahydrofuran.[2] Furthermore, although both *cis*- and *trans*-1,2,3-triphenylcyclopropane react with KO-*t*-Bu–Me_2SO to form a cyclopropyl anion that does not open, the long-lived triphenylcyclopropyl anion generated with *n*-BuLi does undergo ring opening.[3] Because the 1,2,3-triphenylcyclopropyl anion in Me_2SO captures a proton before it opens in a symmetry-allowed manner, it is not reasonable that a cyclopropyl anion from **1** under the same conditions would undergo a symmetry-forbidden reaction.

In addition Newcomb[2] finds that treatment of **1** with *n*-butyllithium in tetramethylethylenediamine followed by quenching with D_2O results in recovery of unrearranged **1** containing deuterium. We confirm that observation, but although Newcomb suggested that result indicated the formation of **5** the deuterium incorporation could have



5

arisen by the known metalation of one or more benzene rings by the powerful metalating agent *n*-BuLi–TMEDA.[4] Dreiding models show that the cyclopropyl proton in **1** is highly hindered by the endo protons at C-6 and C-7, making it extremely difficult for the *n*-BuLi–TMEDA complex to approach it. In our experiments the NMR spectrum of deuterated **1** shows no significant loss of H in the cyclopropyl ring. Although Newcomb has suggested that compound **5** could be initially deuterated at the ortho or para positions of the benzene ring, presumably because of benzylic anion delocalization, this is not necessarily in accord with the preferred sp^3 hybridization of cyclopropyl anions even when they are conjugated with strongly electron withdrawing substituents,[5] nor does it correlate with the reaction of cumylpotassium with D_2O, which does not result in significant ring deuteration.[6]

Apropos of this discussion we report that in contrast to compound **1**, compound **2** reacts with *n*-BuLi–TMEDA, yielding **6a**, **7a**, and **8** as shown in Scheme I.

After 6 h at room temperature in hexane, **2** and *n*-BuLi–TMEDA gave 89% of distilled product $C_{30}H_{31}D$. Preparative scale GLC revealed that 18% of the product was **8**, while the remaining 82% consisted of a mixture of **6a** and **7a**. The ultraviolet and NMR spectra of both deuterated and nondeuterated **6a** and **7a** were compared

(1) Londrigan, M. E.; Mulvaney, J. E. *J. Org. Chem.* **1972**, *37*, 2823.
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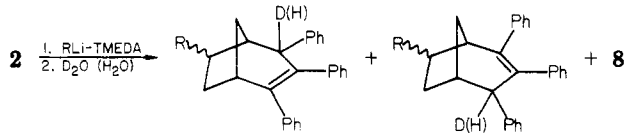
Scheme I



6a. R = *n*-Bu
b, R = Ph

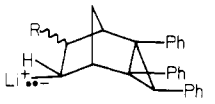
7a, R = *n*-Bu
b, R = Ph

with those of the known compound **3** which confirmed the assigned structures (see Experimental Section).

The minor component **8** is tentatively assigned the structure 2-deuterio-2,3-diphenyl-3-(1-phenylpentyl)bicyclo[2.2.1]-5-heptene on the basis of its NMR spectra (see Experimental Section) and because pyrolysis yields cyclopentadiene and slightly impure PhCh=CPhCHPh-*n*-Bu.

With phenyllithium–TMEDA after 24 h in refluxing benzene compound **2** provided 97% of a mixture of **6b** and **7b**, the structures of which were assigned in a similar manner to **6a** and **7a**.

A possible path for the formation of **6** and **7** involves initial addition of RLi to the olefinic bond in **2** to produce **9** as a TMEDA complex. In support of this we find that



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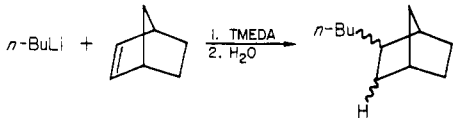
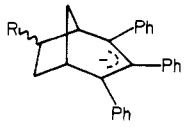
n-BuLi–TMEDA and nonbornene after 6 h at room temperature yield 2-*n*-butylnorbornene (**10**).



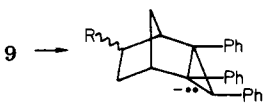
10

The progression from **9** to ring-opened anion **11** which



11

must be the precursor to the mondeuterated products **6** and **7** is open to discussion. For expediency anion **9** has been drawn with the unshared pair of electrons in the endo configuration although it is presumably in rapid equilibrium with the exo isomer. Nevertheless in the endo form the distance from the center of the unshared pair of electrons to the cyclopropyl H is approximately 1.5 Å from Dreiding models. An intramolecular proton transfer via a nonlinear transition state (**9** → **12**) could occur followed by symmetry-forbidden disrotatory cyclopropyl anion opening (**12** → **11**).



12

Experimental Section

2,3,4-Triphenyl-*endo*-tricyclo[3.2.1.0^{2,4}]-6-octene (2), *n*-Butyllithium, and TMEDA in Hexane. To the tricyclic compound (**2**) (2.0 g, 0.00599 mol) and TMEDA (2.1 g, 0.018 mol) in 100 mL of hexane was added *n*-butyllithium (0.0179 mol) in 11.2 mL of hexane. The deep red reaction mixture was stirred at room temperature for 6 h followed by termination with excess deuterium oxide. The reaction mixture was stirred overnight and was then diluted with water and extracted with ether. The combined organic layers were dried over sodium sulfate. Removal of the solvent afforded a yellow oil, which was distilled to give 2.1 g (89%) of a viscous yellow oil, bp 190–195 °C (0.05 torr). The ultraviolet spectrum (95% ethanol) had λ_{max} 260 nm (ϵ 6850). Gas–liquid phase chromatographic analysis (5 ft SE-30, 225 °C) showed three components; 2-deuterio-2,3-diphenyl-3-(1-phenylpentyl)bicyclo-[2.2.1]-5-heptene (**8**, 18%) and the larger component (82%), a mixture of **6a** and **7a** (4-deuterio-6-*n*-butyl-2,3,4-triphenylbicyclo[3.2.1]-2-octene and 4-deuterio-7-*n*-butyl-2,3,4-triphenylbicyclo[3.2.1]-2-octene). The NMR spectrum ($CDCl_3$) of the mixture showed peaks centered at τ 3.10 (m, 15 H) assigned to the aromatic protons; τ 4.50 (s, 1 H) and τ 4.65 (singlet, 3 H) assigned to the vinyl protons of two of the possible stereoisomers of 2-deuterio-2,3-diphenyl-3-(1-phenylpentyl)bicyclo[2.2.1]-5-heptane (**8**); τ 6.65 (m, 0.4 H) assigned to the stilbenyl bridgehead proton of **6a** or **7a**; τ 7.00–8.20 (m, 7 H) assigned to the benzyl protons, bridgehead protons, and methylene protons of **8** the other bridgehead proton, the methylene proton anti to the double bond, the C-7 proton and the exo proton of C-6 of **6a,7a** and the bridgehead protons, the methylene proton anti to the double bond and two C-6 protons of **6a,7a**; τ 8.40–9.30 (m, 11 H) assigned to the *n*-butyl group protons of the three components, the methylene proton syn to the double bond in both **6a,7a** and the endo proton of C-6 **6a,7a** and the C-7 proton of **6a,7a**. Unsaturation tests (bromine and permanganate) were positive.

Preparative GLC (5 ft SE-30, 225 °C) allowed isolation of a mixture of **6a** and **7a**. The NMR spectrum of **6a,7a** was identical with the unseparated mixture with the exception that the protons of **8** were missing.

Anal. Calcd for $C_{30}H_{31}D$: C, 91.60; H, 8.40; 3.22 atom % excess deuterium; mol wt 393. Found: C, 91.27; H, 8.80; 2.94 atom % excess deuterium; m_r (mass spectrum) 393.

When the same reaction was carried out under the same conditions but terminated with water, there was obtained a 95% yield of a mixture of **8** (18%) and **6a,7a** (82%). The NMR spectrum was identical with that of the deuterated compounds with the exception of two new peaks centered at τ 5.5 (t, 0.75 H) assigned to the benzyl proton of the stereoisomers of **6a** in which both the benzyl proton and the *n*-butyl group are endo and τ 6.2 (m, 0.25 H) assigned to the benzyl proton of the stereoisomers of **7a**.

2,3,4-Triphenyl-*endo*-tricyclo[3.2.1.0^{2,4}]-6-octene (2), Phenyllithium, and TMEDA in Benzene. To a solution of the tricyclic compound (2.0 g, 0.00599 mol) and TMEDA (2.8 g, 0.0241 mol) in 50 mL of benzene was added phenyllithium (0.024 mol) in 12 mL of 70:30 benzene–ether. The ether was distilled, and the deep purple solution was refluxed for 24 h. The reaction was terminated by addition of excess deuterium oxide and after the mixture was stirred overnight, it was diluted with water and extracted with ether. The organic layers were dried over sodium sulfate. Removal of the solvent gave an orange oil, which was distilled to give 2.4 g (97%) of a deep orange oil, bp 185–210 °C (0.5 torr). The ultraviolet spectrum (95% ethanol) showed λ_{max} 258 nm (ϵ 10 600). The NMR spectrum showed peaks centered at τ 3.0 (m, 20 H) assigned to the aromatic protons; τ 6.50 (m, 0.7 H) assigned to the stilbenyl bridgehead proton of 4-deuterio-2,3,4,7-tetraphenylbicyclo[3.2.1]-2-octene; τ 7.0–8.4 (m, 5 H) assigned to the other bridgehead proton, the methylene proton anti to the double bond, and the proton of C-6 and C-7 of 4-deuterio-2,3,4,7-tetraphenylbicyclo[3.2.1]-2-octene and the bridgehead protons, the methylene proton anti to the double bond and the C-6 and C-7 protons of 4-deuterio-2,3,4,6-tetraphenylbicyclo[3.2.1]-2-octene; τ 8.7 (m, 1 H) assigned to the methylene proton syn to the double bond in both of the bicyclic compounds.

Anal. Calcd for $C_{32}H_{27}D$: C, 92.97; H, 7.03; 3.57 atom % excess deuterium; mol wt 413. Found: C, 92.91; H, 6.99; 3.22 atom % excess deuterium; m_r (mass spectrum) 413.

When the reaction was carried out by workup with H_2O, there was obtained a 70% yield of a mixture of 2,3,4,7-tetraphenylbicyclo[3.2.1]-2-octene and 2,3,4,6-tetraphenylbicyclo[3.2.1]-2-octene. The NMR spectrum was identical with that of the deuterated compounds with the addition of two new peaks centered at τ 5.3 (t, 0.6 H) assigned to the benzyl proton of the isomer

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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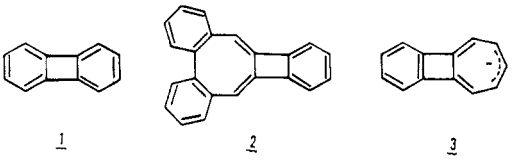
Received May 26, 1981

Analogues of biphenylene (1), in which one benzene ring is replaced by a nonbenzenoid $4n$-π-electron system are of interest as they contain a total of $(4n + 2)$-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



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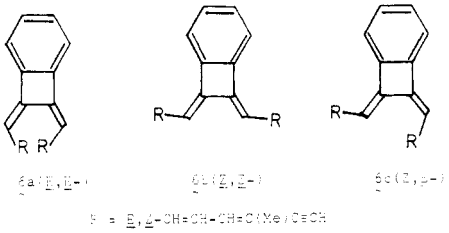
3,[2b] although other compounds are known in which two $4n$-π-electron rings are fused together.[3,4] We have devised an extremely short synthesis of the [16]annulenobiphenylene derivative **7** as shown in the Scheme I. The key step involved the bis-Wittig reaction[5] between 1,2-dihydro-1,2-bis(triphenylphosphoranylidene)benzocyclobutene (**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]

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]

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

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

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(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 $(4n + 2)$-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.

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(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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