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THE 1,7-CYCLOHEXENONORBORNADIENE SYSTEM

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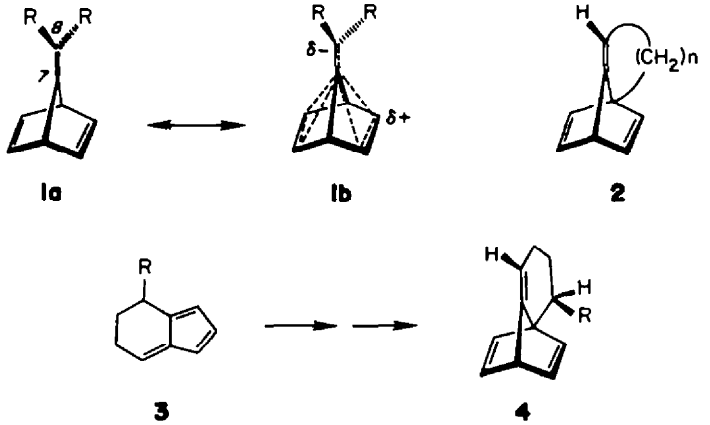
Abstract—2,3-Dimethylene-7-oxabicyclo[2.2.1]heptane, available by reduction and dehydration of the furan–fumaroyl chloride Diels–Alder adduct, undergoes ready dibromocyclopropanation at one of its exocyclic double bonds. The corresponding carbenoid, generated by reaction of the dibromide with 4 equiv of an organolithium reagent, undergoes the Skattebøl rearrangement to provide a fused cyclopentadiene ring which is immediately deprotonated. This anion fragments to a fulvene alkoxide to which the organolithium reagent subsequently adds. The resulting anion, namely **9**, provides fulvenes of type **3** on workup. The use of **3** as a diene in Diels–Alder cycloadditions is demonstrated by the condensation of methyl derivative **3a** with dimethyl acetylenedicarboxylate and (*E*)-1,2-bis(phenylsulfonyl)ethylene. The question of face selectivity is raised. For the bissulfone adducts **21** and **22**, reductive desulfonylation with 1–2% sodium amalgam delivers hydrocarbon **23**, the first known member of the 1,7-cycloalkenonorbornadiene class of molecules. ^{13}C-NMR measurements show that **23** is as polarized as its simple non-annulated prototype and is unstrained.

The parent methylenenorbornadiene molecule (**1**), first synthesized independently in two laboratories somewhat more than a decade ago,[1,2] was immediately recognized to be a unique hydrocarbon. The substance possesses a large dipole moment (0.71 D) and exhibits at strikingly high field (δ 3.63 in $CDCl_3$) a signal attributable to its methylene protons. While these properties are unusual, it is the ^{13}C-NMR and photoelectron (PE) spectra of **1** that manifest most clearly the existence of pronounced homoconjugation. Thus, C-7 in **1** resonates at 177.1 ppm, a record downfield shift for an olefinic C atom.[3] The appearance of C-8 at 78 ppm is considered diagnostic of high charge density at this site, although this conclusion has been contested.[4] The HOMO of **1** is raised by 0.3 eV relative to that in norbornadiene as a direct consequence of crossed longicyclic interaction[5] between the exocyclic double bond and remaining π system. The ultimate consequence is development of bicycloaromatic character and polarization of the C-7/C-8 double bond as in **1b**. These conclusions are supported by CNDO/2 and MINDO/2 calculations.[1]

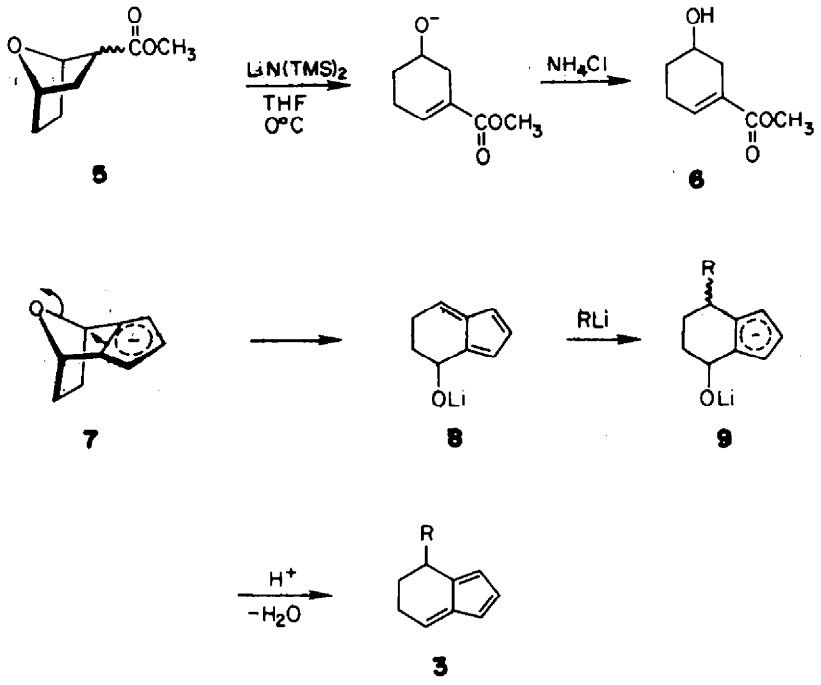
The developments to date in this area have focused primarily on elucidating the response of **1** to the action of uniparticulate[6] electrophiles[2] and to the preparation of derivatives substituted at C-8 with electron-donating and -withdrawing groups.[4] In our view, annulated methylenenorbornadienes of type **2** could prove to be informative molecules. Clearly, as the size of *n* is reduced, some warping of the parent framework must develop. Although the extent to which incremental enhancement of the strain energy by this means would perturb electronic interaction within this particular π system is unknown, special interest would accrue to the resultant spectral changes. Furthermore, if substances possessing these structural features were available, several interesting mechanistic problems could be addressed.

Prior to the present effort,[7] no annulated trienes of general formula **2** were known.[8] Several 1,7-alkenonorbornanes have recently commanded attention,[9–12] but of course the synthetic routes utilized to gain access to these systems are not extendable to **2**. Accordingly, we set out to develop a protocol capable of giving rise to 1,7-cyclohexenonorbornadienes (**2**, $n = 3$), the first members of this series.

Our strategy envisioned completion of the requisite framework construction by Diels–Alder addition of an acetylene synthon[13] to fulvenes such as **3**.[14] The presence of the R group was to allow for suitable distinction between the two faces of the fulvene, to provide adequate scope to the process, and to cause the



1a **1b** **2** **3** **4**



two endocyclic double bonds in **4** to be recognizably different.

On this basis, the present investigation was reduced to developing a feasible route to **3**. In this connection, the ability of 7-oxabicyclo[2.2.1]heptenes and -heptanes to undergo base-promoted retrograde Michael reactions under mild conditions gave evidence of promise.[15] The conversion of **5** to **6** is illustrative. The versatility of the approach rests upon the ready availability of the starting materials via [4+2] cycloaddition to furans. The extrapolation in thought centered on cyclopentadienide anion **7**, whose fragmentation as indicated would relieve bicyclic strain and deliver **8**. The ultimate intention was not to isolate **8** but more simply to cause this alkoxide to react further with an organolithium reagent of choice to give **9**. Ejection of the oxygenated functionality in **9** would complete the conversion to **3**. This pivotal step would presumably occur by dehydration during the workup process.

A straightforward route to **7** appeared to reside in the Skattebøl rearrangement,[16] notwithstanding its less than predictable serviceability in strained bicyclic systems.[17] Preparation of the requisite 2,3-dimethylene-7-oxabicyclo[2.2.1]heptane precursor (**12**) was realized by direct application of the general procedure developed by Butler and Snow.[18] Thus, condensation of equimolar amounts of furan and fumaroyl chloride at 0° in the absence of solvent[19] provided adduct **10** in quantitative yield. Use of solvent as previously directed[20] led to equilibrium mixtures containing much less (~33%) of the desired product. Although cold storage of these mixtures resulted in a shift toward **10** in the equilibrium, the aforementioned solvent-free process enjoys significantly greater preparative value. A comparable equilibration has been previously noted in the Diels–Alder cycloaddition of dimethyl fumarate to furan.[21]

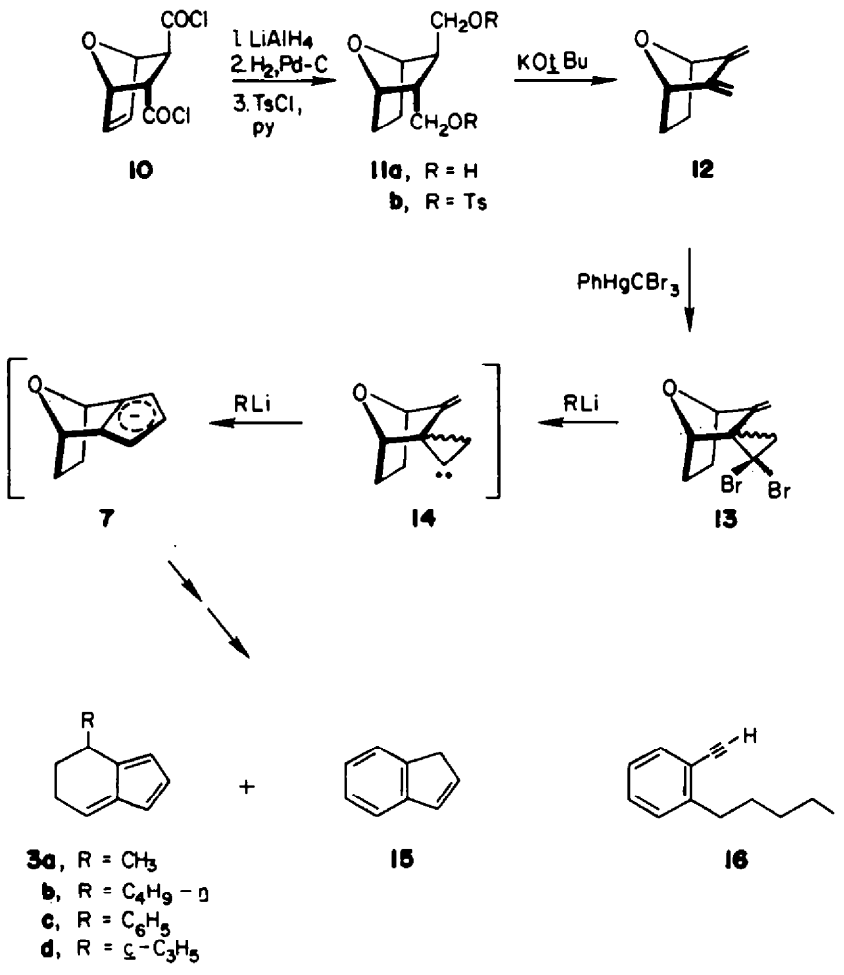
Immediate reduction of **10** with lithium aluminum hydride provided diol **11a** efficiently.† Subsequent catalytic hydrogenation, bis-tosylation, and twofold elimination with potassium t-butoxide furnished **12** as a colorless oil.[22] Heating **12** with 1 equiv of phenyl(tribromomethyl)mercury[23,24] afforded a 3:1 mixture of stereoisomeric dibromocyclopropanes **13** in good yield.

Reaction of **13** with 4 equiv of methyllithium in ether at room temperature, conditions now viewed as typical for the Skattebøl rearrangement,[16,25] gave rise after workup by silica gel chromatography to **3a** (8%) and indene (**15**, 1%) as the only high R_f components. The remainder of the reaction mixture consisted of a number of higher polarity products possessing hydroxyl substitution. When several attempts to convert this global ensemble to **3a** by various dehydration methods were to no avail, further characterization of the individual dehydration methods was not pursued.

Hydrocarbon **3a**, the first reported example of a 5,6-dihydro-4H-indene,[14] is a yellow oil having an exceedingly bright iridescence. Its ^{1}H- and ^{13}C-NMR spectra (Experimental) are characterized by well separated signals that are fully diagnostic of, and consistent with, the structural assignment. Additional confirmatory evidence can be found in its reactivity under Diels–Alder conditions as described subsequently.

The generality of this process was demonstrated by entirely comparable exposure of **13** to n-butyllithium, phenyllithium, and cyclopropyllithium. The resultant bright yellow substances **4b–d** were isolated with equal ease in 6–12% yield. Although the absolute yields of the fulvenes are low, the reactions are readily amenable to

† Katsube and co-workers[20] have reported the preparation of **11a** by reduction of the dimethyl ester of **10**; however, no analytical data was presented.



10 11a, R = H; b, R = Ts 12 7 14 13

3a, R = CH_3
b, R = C_4H_9-n
c, R = C_6H_5
d, R = c-C_3H_5

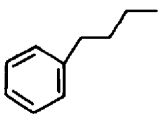
15 16

scale-up and the preparation of relatively large amounts has proven quite feasible.

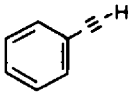
In the n-butyllithium example, a significantly larger than normal amount of indene is formed (18%). A third hydrocarbon identified as the acetylene **16** (6%) is also produced. The presence in **16** of a terminal triple bond was suggested by IR absorptions at 3310 and 2100 cm^{-1}.[26] Gated decoupled ^{13}C-NMR measurements provided the anticipated acetylenic C—H coupling constants of 250.4 Hz[27a] for the terminal carbon and 49.1 Hz (long-range coupling)[27b] for the internal sp-hybridized carbon. Off-resonance ^{13}C-NMR and ^{13}C–^{1}H correlation studies permitted assembling of the entire carbon skeleton. In particular, *ortho* substitution of the benzene ring, indicated by a strong IR band at 760 cm^{-1}, was confirmed by ^{1}H decoupling. Actually, the chemical shifts of the benzenoid carbons within **16** can be closely approximated by suitable weighting of the shifts present in the two model systems n-butylbenzene[27c] and phenylacetylene.[27d] The point of reference is benzene (^{13}C = 128.5 ppm). The relevant information is contained in the formulas that follow.

A reasonable hypothetical mechanism for the formation of **16** centers about alternative conversion (in part) of carbenoid **14** to vinylallene **18**.[28] Attack of n-butyllithium on **18** to cleave the oxygen bridge leads to **19** with the n-pentyl side chain suitably appended. The subsequent dehydration and oxidation of **19** to produce **16** can occur during processing of the reaction mixture. The allene–acetylene isomerization is certainly a well-recognized phenomenon.

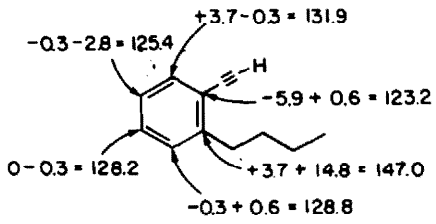
Next, the **3** → **4** conversion was specifically



C_1	C_2	C_3	C_4
143.3	129.1	128.2	125.7
+14.8	+0.6	−0.3	−2.8

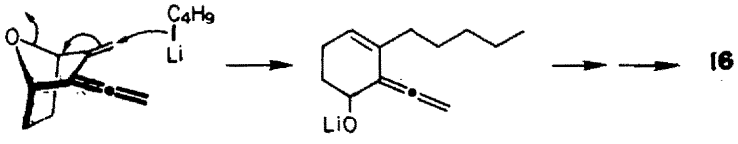


122.6	132.2	128.2	128.5
−5.9	+3.7	−0.3	0



17

calcd. for **17**	obsd. for **16**
147.0	145.61
131.9	132.86
128.8	128.74
128.2	128.70
125.4	125.51
123.2	121.45



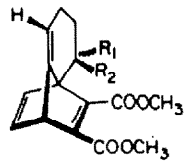
18 19

addressed. In a preliminary experiment designed to gauge the dienic reactivity of **3a**, the fulvene was allowed to stand with dimethyl acetylenedicarboxylate in chloroform solution at room temperature for 6 days. During this time, [4+2] cycloaddition occurred with greater than 95% efficiency to provide an 85 : 15 mixture of **20a** and **b**. The stereochemical assignments are based upon the assumed preferential approach of the dienophile from the less hindered surface of **3a**.

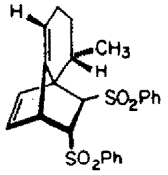
In analogous fashion, **3a** was exposed to (*E*)-1,3-bis(phenylsulfonyl)ethylene[29] in dichloromethane solution during 48 hr at 20°. An inseparable 70 : 30 mixture of **21** and **22** was isolated in 71% yield. A very minor amount of the remaining two isomeric possibilities was also detected. A series of proton decoupling experiments permitted unambiguous structural assignment to the pair of major disulfones. For example, the absence of spin–spin interaction between the bridgehead and neighboring α-sulfonyl protons in **22** requires that the $PhSO_2$ group bonded thereto have an exo disposition. The methyl orientation in **21** and **22** has again been assigned so as to place it more remote from the sulfonyl substituents. However, this particular stereochemical issue is inconsequential to our goal since subsequent buffered sodium amalgam reduction[3] of the mixture of disulfones led efficiently to **23**.

The ^{1}H-NMR spectrum of **23** reflects the dissymmetry introduced by the methyl group. Its ^{13}C-NMR parameters support the conclusion that homoconjugative interaction between the individual π segments is fully operational. Thus, the chemical shift of C-7 appears at 171.3 ppm, shifted upfield to the extent of 5.8 ppm relative to that of **1** (R = H). This level of shielding conforms nicely to the monoalkyl substitution plan at C-8, since C-7 in **1** (R = CH_3) is seen at 165.7 ppm.[4] In fact, the incremental Δppm values of 5.6–5.8 indicate that **23** is strain free as suggested by molecular models.

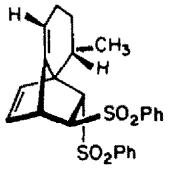
Among the potential applications of 1,7-cyclohexenonorbornadienes such as **23** is the possibility that they might serve as precursors to quadricyclanes[30] having two quite different cyclopropane ring substitution plans. In addition, the R substituent in the laterally fused cyclohexene ring of these valence isomers can be utilized to probe possible long-range electronic and/or steric control of cycloaddition reactions involving electron-deficient olefinic partners.[31] A particularly interesting variant of this chemistry would involve structural analogues wherein the dienophile is tethered by a carbon chain to the cyclohexene ring so as to permit intramolecular bonding between the linked structural elements.



20a, $R_1 = CH_3$, $R_2 = H$
b, $R_1 = H$, $R_2 = CH_3$



21



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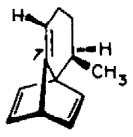

23

EXPERIMENTAL

(2 - *endo*,3 - *exo*) - 7 - *Oxabicyclo*[2.2.1]*hept* - 5 - *ene* - 2,3 - *bis*(*carbonyl chloride*) (**10**)

Freshly distilled fumaryl chloride (77 g, 0.5 mol) was added dropwise to freshly distilled furan (34 g, 0.5 mol) at 0°. After 30 min at the same temp, the mixture solidified to afford a quantitative yield of **10** as colorless prisms; 90 MHz ^{1}H-NMR ($CDCl_3$, δ) 6.70–6.45 (m, 2H), 5.42 (m, 2H), 4.08 (m, 1H), 3.32 (d, J = 4 Hz, 1H). This material was directly reduced.

(2 - *endo*,3 - *exo*) - 7 - *Oxabicyclo*[2.2.1]*hept* - 5 - *ene* - 2,3 - *dimethanol*

Powdered **10** (111 g, 0.5 mol) was added cautiously in small portions to a stirred slurry of LAH (38.0 g, 1.0 mol) in 1 : 1 tetrahydrofuran–ether (1050 ml) at 0°. The mixture was stirred at 0° for 3 hr and at 20° for 15 hr and subsequently quenched with 20% KOH aq (150 ml) and water (150 ml). The organic

soln was decanted, dried, and evaporated to afford 31.5 g (41%) of diol as a colorless oil. Continuous extraction of the Al salts with ether for 18 hr provided an additional 3.6 g of product to give an overall yield of 88%; IR (neat, cm^{-1}) 3450, 3000, 2920, 2875, 1405, 1315, 1080, 1025, 895; 90 MHz ^{1}H-NMR (CD_3COCD_3, δ) 6.33 (m, 2H), 4.81 (m, 1H), 4.69 (m, 1H), 3.70–3.10 (series of m, 6H), 2.00–1.18 (series of m, 2H); 20 MHz ^{13}C-NMR (CD_3COCD_3, ppm) 137.17, 134.11, 80.64, 80.31, 65.16, 64.67, 46.96, 46.19; mass spectrum m/z (M^+) calc 120.0575, obsd 120.0555.

(2 - *endo*,3 - *exo*) - 7 - *Oxabicyclo*[2.2.1]*heptane* - 2,3 - *dimethanol* (**11a**)

A soln of the above diol (42.3 g, 0.27 mol) in MeOH (150 ml) containing 10% Pd–C (1.5 g) was hydrogenated at 50 psi until H_2 consumption ceased. After filtration of the catalyst, solvent was removed *in vacuo* to give 40.4 g (94%) of **11a** as a colorless oil; IR (neat, cm^{-1}) 3450, 2970, 2920, 2880, 1190, 1090, 1040, 970; 90 MHz ^{1}H-NMR (CD_3COCD_3, δ) 4.60–3.20 (series of m, 8H), 2.30–1.10 (series of m, 6H); 20 MHz ^{13}H-NMR (CD_3COCD_3, ppm) 78.95, 78.83, 65.29, 63.23, 51.64, 49.94, 30.40, 24.75; mass spectrum m/z ($M^+ - H_2O$) calc 140.0838, obsd 140.0809.

(2 - *endo*,3 - *exo*) - 7 - *Oxabicyclo*[2.2.1]*heptane* - 2,3 - *dimethanol bis*(4 - *methylbenzenesulfonate*) (**11b**)

A soln of **11a** (20.0 g, 0.13 mol) in pyridine (50 ml) was added dropwise to a stirred, cooled (0°) soln of *p*-toluenesulfonyl chloride (53.1 g, 0.27 mol) and 4-dimethylaminopyridine (100 mg) in pyridine (200 ml). The mixture was stirred at 20° for 15 hr, diluted with ice water (400 ml) and extracted with CH_2Cl_2 (2 × 200 ml). The combined organic extracts were washed with 10% H_2SO_4 aq (3 × 100 ml) and water (until neutral) prior to drying and evaporation to yield 45.5 g (75%) of **11b** as an almost colorless oil that solidified upon standing, m.p. 114–115° (from MeOH); IR ($CHCl_3$, cm^{-1}) 2980, 2920, 1598, 1360, 1190, 1175, 1095, 955, 810; 90 MHz ^{1}H-NMR ($CDCl_3$, δ) 7.75 (m, 4H), 7.34 (m, 4H), 4.52–3.68 (series of m, 6H), 2.45 (s, 6H), 2.00–1.20 (m, 6H); 20 MHz ^{13}C-NMR ($CDCl_3$, ppm) 145.20, 145.10, 132.90, 132.79, 130.06, 127.93, 78.07, 77.90, 71.12, 69.70, 46.85, 44.77, 29.19, 23.94, 21.65; mass spectrum m/z (M^+) calc 466.1120, obsd 466.1132.

2,3 - *Dimethylene* - 7 - *oxabicyclo*[2.2.2]*heptane* (**12**)

A soln of **11b** (20.0 g, 0.043 mol) in anhyd THF (300 ml) was treated with t-BuOH (14.4 g, 0.13 mol) and stirred at 20° for 15 hr. The mixture was diluted with ice water (300 ml) and extracted with CH_2Cl_2 (3 × 300 ml). The combined organic extracts were washed with 10% HCl aq (3 × 100 ml), 5% $NaHCO_3$ aq (1 × 100 ml), and water (until neutral), then dried and evaporated to yield a dark yellow oil. Bulb-to-bulb distillation of this residue provided 2.6 g (50%) of **12** as a colorless oil, b.p. < 200° at 35 Torr; IR ($CDCl_3$, cm^{-1}) 3097, 2965, 1653, 1462, 1423, 1300, 1248, 1194, 987; 90 MHz ^{1}H-NMR ($CDCl_3$, δ) 5.17 (s, 2H), 4.89 (s, 2H), 4.80 (m, 2H), 2.10–1.20 (series of m, 4H); 20 MHz ^{13}C-NMR ($CDCl_3$, ppm) 148.65, 100.37, 81.07, 29.35.

2,2 - *Dibromo* - 3' - *methylenespiro*[*cyclopropane* - 1,2' - [7]*oxabicyclo*[2.2.1]*heptane*] (**13**)

A mixture of **12** (1.0 g, 0.008 mol) and phenyl(tribromomethyl)mercury (4.3 g, 0.008 mol) in anhyd benzene (10 ml) was heated to reflux for 6 hr. After cooling, the precipitated phenylmercuric bromide was filtered, and the filtrate was passed through a column of neutral alumina (elution with benzene (300 ml)). Evaporation of solvent provided 2.1 g (89%) of a 3 : 1 mixture of isomers of **13** as a pale yellow oil; IR (neat, cm^{-1}) 2990, 2955, 1668, 1427, 1343, 1295, 1192, 1165, 1010, 870; 300 MHz ^{1}H-NMR ($CDCl_3$, δ) 5.13 (s, 0.75H), 5.02 (s, 0.75H), 5.00 (s, 0.25H), 4.99 (s, 0.25H), 4.77 (d, J = 4.8 Hz, 0.75H), 4.71 (s, 0.25H), 4.68 (s, 0.75H), 4.36 (d, J = 4.6 Hz, 0.25H), 2.31–1.65 (series of m, 6H); 20 MHz ^{13}C-NMR ($CDCl_3$, ppm) 150.95, 104.31, 103.93, 84.47, 84.14, 83.81, 81.79, 44.01, 42.93, 37.61, 35.59, 32.65, 31.16, 30.56, 28.81, 27.55, 26.30.

4-*Methyl*-5,6-*dihydro*-4H-*indene* (**3a**)

A 1.57 M soln of MeLi (26 ml, 0.041 mol) in ether was added to a soln of **13** (3.0 g, 0.010 mol) in the same solvent (300 ml). The mixture was stirred for 15 hr at 20° and poured into ice water (150 ml). The organic layer was separated, the aqueous phase was extracted with ether (2 × 100 ml), and the combined organic solns were washed with water (until neutral), dried, and evaporated to yield a dark yellow oil. Preparative thin layer silica gel chromatography of the residue (elution with pentane) provided 109 mg (8%) of **3a** as a yellow oil; IR (neat, cm^{-1}) 3075, 2960, 2928, 1655, 1495, 1425, 1345, 925, 818, 750, 675; 300 MHz ^{1}H-NMR ($CDCl_3$, δ) 6.74 (m, 1H), 6.46 (m, 1H), 6.13–6.10 (m, 2H), 2.70–2.60 (m, 1H), 2.53–2.37 (m, 2H), 1.91–1.85 (m, 1H), 1.55–1.41 (m, 1H), 1.25 (d, J = 3.9 Hz, 3H); 20 MHz ^{13}C-NMR ($CDCl_3$, ppm) 144.82 (s), 139.65 (s), 138.37 (d), 132.24 (d), 122.02 (d), 119.34 (d), 33.86 (t), 30.22 (d), 26.97 (t), 19.36 (q); mass spectrum m/z (M^+) calc 132.0939, obsd 132.0906.

Reaction of **13** *with* n-*butyllithium*

A 0.25 M soln of freshly prepared n-BuLi (65 ml, 0.016 mol) in ether was added to a soln of **13** (1.2 g, 0.0041 mol) in the same solvent (200 ml). The mixture was stirred at 20° for 15 hr and poured into ice water (150 ml). The organic layer was separated, the aqueous phase was extracted with ether (2 × 100 ml), and the combined organic solns were washed with water (until neutral), dried, and evaporated to provide a light orange oil. Preparative thin layer silica gel chromatography of the residue (elution with pentane) afforded 36 mg (16%) of **16** and 54 mg of a 1 : 3 mixture of **3b** (6%) and indene (**15**, 18%).

For **3b**: 300 MHz ^{1}H-NMR ($CDCl_3$, δ) 6.74 (m, 1H), 6.47 (m, 1H), 6.12 (m, 2H), 2.60–2.34 (series of m, 3H), 2.07–1.95 (m, 1H), 1.85–1.70 (m, 1H), 1.58–1.29 (series of m, 6H), 0.95 (t, J = 6.9 Hz, 3H); 20 MHz ^{13}C-NMR ($CDCl_3$, ppm) 138.44, 133.63, 132.27, 132.16, 122.48, 119.47; mass spectrum m/z (M^+) calc 174.1406, obsd 174.1417.

For **16**: IR (neat, cm^{-1}) 3310, 3080, 3035, 2975, 2940, 2875, 2110, 1490, 1470, 1385, 755; 300 MHz ^{1}H-NMR ($CDCl_3$, δ) 7.48–7.12 (series of m, 4H), 3.23 (s, 1H), 2.79 (t, J = 7.8 Hz, 2H), 1.67–1.62 (m, 2H), 1.37–1.32 (m, 4H), 0.92–0.87 (m, 3H); 300 MHz ^{13}C-NMR ($CDCl_3$, ppm) 145.61 (s), 132.86 (d), 128.74 (d), 128.70 (d), 125.51 (d), 121.45 (s), 82.50 (d), 80.36 (d), 34.45 (t), 31.67 (t), 30.31 (t), 22.51 (t), 14.03 (q); mass spectrum m/z (M^+) calc 172.1252, obsd 172.1276.

4-*Phenyl*-5,6-*dihydro*-4H-*indene* (**3c**)

A 0.93 M soln of freshly prepared PhLi (13.7 ml, 0.015 mol) in ether was added to a soln of **13** (1.2 g, 0.0041 mol) in the same solvent (250 ml). The mixture was stirred at 20° for 15 hr and poured into ice water (150 ml). The organic layer was separated, the aqueous phase was extracted with ether (2 × 100 ml), and the combined organic solns were washed with water (until neutral), dried, and evaporated to provide a light orange oil. Purification using preparative thin layer silica gel chromatography (elution with pentane) gave 74 mg (9%) of **3c** as bright yellow crystals, m.p. 165–166° (from EtOH); IR (near, cm^{-1}) 3040, 2930, 1650, 1495, 1455, 1343, 1075, 855, 763; 300 MHz ^{1}H-NMR ($CDCl_3$, δ) 7.52–7.19 (m, 5H), 6.86 (m, 1H), 6.49 (m, 1H), 6.25 (m, 1H), 5.87 (s, 1H), 3.92–3.88 (m, 1H), 2.64–2.49 (m, 2H), 2.22–1.97 (m, 2H); 20 MHz ^{13}C-NMR ($CDCl_3$, ppm) 145.43, 144.77, 138.38, 137.12, 132.36, 128.32, 128.04, 126.35, 125.04, 119.79, 42.54, 34.06, 26.84; mass spectrum m/z (M^+) calc 194.1095, obsd 194.1087.

4-*Cyclopropyl*-5,6-*dihydro*-4H-*indene* (**3d**)

A 0.45 M soln of freshly prepared cyclopropyllithium (19.0 ml, 0.0086 mol) in ether was added to a soln of **13** (0.63 g, 0.0021 mol) in the same solvent (125 ml). The mixture was stirred at 20° for 14 hr and poured into ice water (75 ml). The organic layer was separated, the aqueous phase was extracted with ether (2 × 50 ml), and the combined organic solns were washed with water (until neutral), dried, and evaporated. Purification of the resulting oil using preparative thin layer silica gel chromatography (elution with pentane) provided 40 mg (12%)

of **3d** as a bright yellow oil; IR (neat, cm^{-1}) 3090, 3010, 2930, 2860, 2815, 1650, 1495, 1430, 1345, 1015, 815, 755; 300 MHz ^{1}H-NMR ($CDCl_3$, δ) 6.74 (m, 1H), 6.48 (m, 1H), 6.34 (m, 1H), 6.15 (m, 1H), 2.63–2.52 (m, 1H), 2.45–2.33 (m, 1H), 2.16–1.99 (m, 1H), 1.82–1.60 (m, 2H), 0.93–0.79 (m, 1H), 0.67–0.58 (m, 1H), 0.55–0.40 (m, 1H), 0.39–0.27 (m, 1H), 0.21–0.08 (m, 1H); 75 MHz ^{13}C-NMR ($CDCl_3$, ppm) 138.63, 138.48, 137.78, 132.32, 122.95, 119.44, 40.95, 31.73, 26.91, 15.33, 4.30, 2.06; mass spectrum *m/z* (M^+) calc 158.1095, obsd 158.1079.

Cycloaddition of **3a** *with dimethyl acetylenedicarboxylate*

A soln of **3a** (30 mg, 0.23 mmol) and dimethyl acetylenedicarboxylate (32 mg, 0.23 mmol) in chloroform-*d* (0.4 ml) was kept at 20° for 6 days. Solvent was removed *in vacuo*, and the resulting oil was purified using medium pressure liquid chromatography on silica gel (elution with 5% EtOAc in petroleum ether) to provide 35 mg (95% based on recovered dimethyl acetylenedicarboxylate) of a mixture of **20a** and **b** in a ratio of 85 : 15 as determined from the 300 MHz ^{1}H-NMR spectrum.

For **20a**: 300 MHz ^{1}H-NMR ($CDCl_3$, δ) 7.08–7.03 (m, 1H), 6.97 (d, J = 5.4 Hz, 1H), 4.56 (t, J = 4.1 Hz, 1H), 4.26 (d, J = 3.0 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 2.31–2.22 (m, 1H), 1.89–1.81 (m, 2H), 1.68–1.60 (m, 1H), 1.33–1.23 (m, 1H), 1.18 (d, J = 6.9 Hz, 3H); 20 MHz ^{13}C-NMR ($CDCl_3$, ppm) 167.43 (s), 167.26 (s), 163.72 (s), 158.63 (s), 147.82 (s), 144.43 (d), 142.01 (d), 94.35 (d), 66.44 (s), 52.70 (q), 52.06 (d), 51.93 (q), 30.34 (t), 28.43 (d), 21.02 (t), 18.14 (q); mass spectrum *m/z* (M^+) calc 274.1205, obsd 274.1213.

Cycloaddition of **3a** *with* (*E*) - 1,2 - *bis(phenylsulfonyl)ethylene*

A mixture of **3a** (133 mg, 1.0 mmol) and (*E*)-1,2-bis(phenylsulfonyl)ethylene in CH_2Cl_2 (3 ml) was stirred at 20° for 48 hr. Filtration of unreacted dienophile followed by evaporation of solvent provided a light yellow oil. Purification of the residue by medium pressure liquid chromatography on silica gel (elution with 33% EtOAc in petroleum ether) gave 198 mg (71% based on recovered bis(phenylsulfonyl)ethylene) of a 70 : 30 mixture of **21** and **22**.

For (1*S**,2*S**,7*R**,8*S**,9*S**) - 2 - *methyl* - 8,9 - *bis(phenylsulfonyl)tricyclo*[6.2.2.0^{1,6}]undeca - 5,10 - diene (**21**): 300 MHz ^{1}H-NMR ($CDCl_3$, δ) 7.94–7.48 (m, 10H), 6.59 (d, J = 5.8 Hz, 1H), 6.30 (dd, J = 5.8 and 3.3 Hz, 1H), 4.92 (m, 1H), 4.10 (d, J = 4.9 Hz, 1H), 3.81 (d, J = 4.8 Hz, 1H), 3.42 (d, J = 3.3 Hz, 1H), 2.71–2.63 (m, 1H), 1.87–1.58 (m, 4H), 1.46–1.41 (m, 2H), 1.05 (d, J = 7.1 Hz, 3H); 20 MHz ^{13}C-NMR ($CDCl_3$, ppm) 146.85, 139.58, 138.98, 136.95, 134.82, 133.95, 133.78, 129.24, 128.92, 128.48, 109.78, 70.69, 69.00, 58.06, 47.56, 27.34, 26.41, 19.08, 16.46.

For (1*S**,2*S**,7*R**,8*R**,9*R**) - 2 - *methyl* - 8,9 - *bis(phenylsulfonyl)tricyclo*[6.2.2.0^{1,6}]*undeca* - 5,10 - *diene* (**22**): 300 MHz ^{1}H-NMR ($CDCl_3$, δ) 7.94–7.48 (m, 10H), 6.65 (dd, J = 5.8 and 2.7 Hz, 1H), 6.40 (d, J = 5.9 Hz, 1H), 5.20 (m, 1H), 4.27 (dd, J = 5.4 and 3.4 Hz, 1H), 3.99 (d, J = 5.4 Hz, 1H), 3.51 (t, J = 3.1 Hz, 1H), 2.71–2.63 (m, 1H), 2.02–1.82 (m, 2H), 1.46–1.41 (m, 2H), 0.71 (d, J = 6.8 Hz, 3H).

2 - *Methyl* - *tricyclo*[6.2.2.0^{1,6}]*undeca* - 5,8,10 - *triene* (**23**)

A soln of a 70 : 30 mixture of **21** and **22** (115 mg, 0.26 mmol) in anhyd MeOH (6 ml) containing disodium hydrogen phosphate (0.6 g) was purged with N_2. With efficient stirring, 1–2% sodium amalgam (*ca* 1 g) was added in portions. After 3 hr, the mixture was filtered through a Celite pad, poured into brine (10 ml), and extracted with pentane (3 × 10 ml). The combined organic extracts were washed with water (until neutral), dried, and freed of solvent. Gravity flow silica gel chromatography (elution with pentane) of the residue provided 30 mg (73%) of **23** as a colorless oil; IR (neat, cm^{-1}) 3080, 3015, 2975, 2940, 1715, 1540, 1471, 1463, 1340, 1330, 840, 805, 710, 695; 300 MHz ^{1}H-NMR ($CDCl_3$, δ) 6.96–6.90 (m, 3H), 6.73 (d, J = 5.2 Hz, 1H), 4.31 (t, J = 3.8 Hz, 1H), 3.88 (m, 1H), 2.10–2.00 (m, 1H), 1.84 (dt, J = 7.7 and 3.8 Hz, 2H), 1.63 (ddt, J = 12.9, 3.6 and 3.6 Hz, 1H), 1.32–1.19 (m, 1H), 1.26 (d, J = 6.9 Hz, 3H); 75 MHz ^{13}C-NMR ($CDCl_3$, ppm) 171.29, 145.95, 144.48, 143.72, 143.09, 88.88, 62.50, 52.08, 31.09, 30.35, 22.07, 18.62; mass spectrum *m/z* (M^+) calc 158.1096, obsd 158.1089.

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