103. PE Spectra of *Dewar* Benzenes, Bridged by a Cyclohexadiene or a Butadiene Unit

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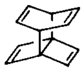
The electronic structure of [4.2.2]propella-2,4,7,9-tetraene (**1**), 2,5-etheno[4.2.2]propella-3,7,9-triene (**2**), and of several hydrogenated derivatives of **2** has been investigated using He(I) PE spectroscopy and MO calculations. It is found that in **2** the 1,4-cyclohexadiene moiety interacts considerably with the bicyclo[2.2.0]hexadiene unit, while in **1** the interaction between the butadiene fragment and the *Dewar* benzene unit is minute. The syntheses of **3**–**5** are reported.

1,4-Bridged *Dewar* benzenes are of interest because of their rearrangement into cyclophanes [1], and their structural [2] and electronic properties [3]. An investigation of bicyclo[2.2.0]hexadiene (*Dewar* benzene) and some of its derivatives showed that the ordering of the π-MO's depends considerably on the substituents. For the parent compound, the sequence $5b_2$ above $8a_1$ seems likely, but for the hexamethyl derivative of *Dewar* benzene the sequence is reversed.

1



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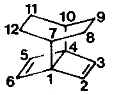

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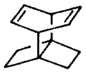

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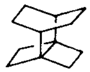
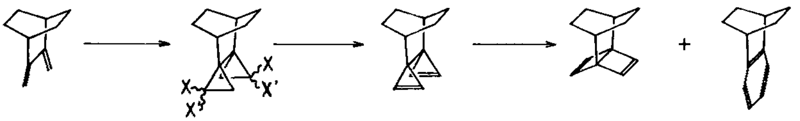


5

We have investigated [4.2.2]propella-2,4,7,9-tetraene (**1**), 2,5-etheno[4.2.2]propella-3,7,9-triene (**2**) as well as several hydrogenated products of **2**, **3**–**5** [4], by means of He(I) PE spectroscopy. In compounds **1**, **2**, and **3**, the 1,4-positions of *Dewar* benzene are bridged by a butadiene unit, a 1,4-cyclohexadiene fragment, or a cyclohexane unit, respectively. Finally **4** and **5** are examples where a bicyclo[2.2.0]hexane unit is bridged by a cyclohexadiene (**4**) or a cyclohexane moiety, respectively. To assign the PE spectra of **1**–**5**, we have carried out MO calculations.

Synthesis. – The preparation of compounds **1** and **2** has been reported in [4]. Compound **3** was synthesized according to the method of *Bickelhaupt* and coworkers [5] (*Scheme 1*). The treatment of **6** [6] with $CHBr_3$/50% aq. NaOH/hexadecyltrimethylammonium bromide [7] at *ca.* 5° afforded bis(dibromocarbene) adduct **7a** in 33% yield, which was subsequently reduced with Bu_3SnH [8] to give a mixture of dibromides **7b**. Dehydrobromination of **7b** by *t*-BuOK in DMSO gave **8**, which provided **3** together with **9** upon treatment with $AgClO_4$ in $MeNO_2$ [5]. Catalytic hydrogenation of **3** afforded **5**.

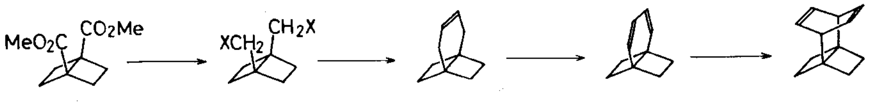
Scheme 1



6 **7a** X = X' = Br
b X = H, X' = Br **8** **3** **9**

The preparation of **4** was carried out as depicted in *Scheme 2*. $LiAlH_4$ reduction of **10** [9] followed by reaction with $MsCl/Et_3N$ gave bismethanesulfonate **11b** which was treated with NaCN in DMF to give **11c**. Reduction of **11c** with $(i\text{-}Bu)_2AlH$ and the *McMurry* coupling [10] of resultant dialdehyde **11d** produced **12**. Bromination of **12** and the subsequent dehydrobromination afforded **13**, which was successively treated with maleic anhydride and $Ni(CO)_2(Ph_3P)_2$ [11] to give **4**.

Scheme 2

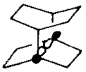


10 **11a** X = OH
b X = OSO_2Me
c X = CN
d X = CHO **12** **13** **4**

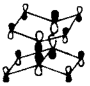
Spectroscopic Results. – The PE spectra of **1**–**5** are shown in *Fig. 1*, and vertical ionization energies in the *Table*.

For the discussion of the electronic structure of the molecules of **1**–**5**, it was necessary to calculate their structural parameters. This was achieved by energy minimization with respect to all internal coordinates using the MNDO procedure [12].

Interpretation. – We start our interpretation, using *Koopmans'* theorem [14], by considering the PE spectrum of **5**. It shows three bands between 8 and 10 eV (see *Fig. 1*). The MNDO [12] or a *Hartree Fock ab initio* method using a minimal basis set (STO 3G) [15] yields the result that for **5** the orbital sequence should be $15a_1$, $8a_2$, and $12b_1$.


$15a_1$


$8a_2$


$12b_1$

Whereas $15a_1$ is mainly localized in the bridgehead σ bond of the bicyclo[2.2.0]hexane part, $8a_2$ and $12b_1$ are more delocalized. The MO $8a_2$ can be described as the antibonding linear combination of the strongly delocalized ribbon orbitals of the cyclohexane ring [16] and of the bicyclo[2.2.0]hexane moiety. The orbital $12b_1$ is localized mainly on the two σ bonds, connecting the two ring moieties with some C–H σ-participation.

Since the ionization energies calculated for the first few PE bands of **1**–**4** are not satisfactory, we shall first discuss their PE spectra qualitatively by comparing them with those of related compounds, *e.g.* *Dewar* benzene [3] or bicyclo[2.2.2]octadiene [17].

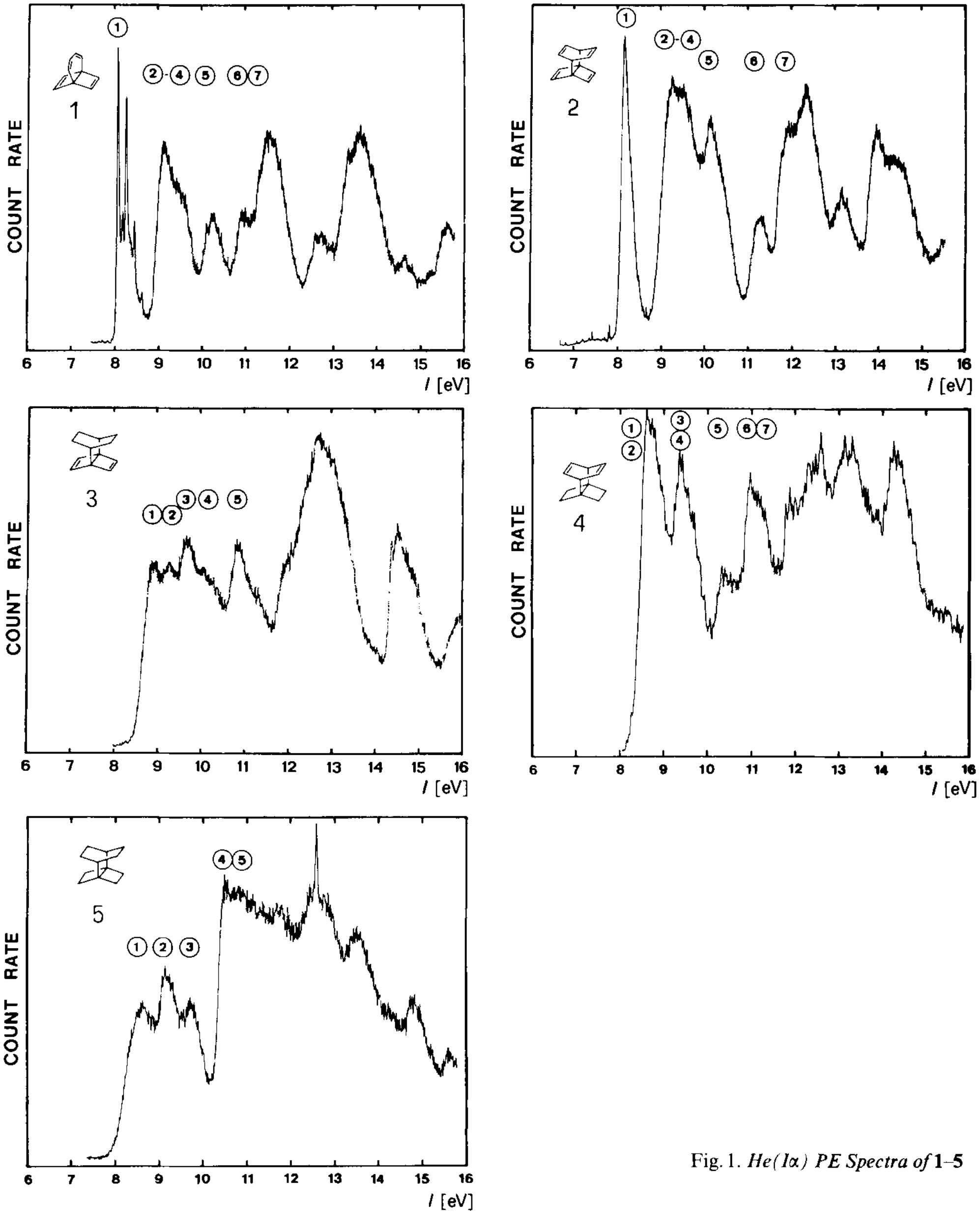


Fig. 1. *He(Iα) PE Spectra of* **1**–**5**

The PE Spectrum of 4. – The PE spectrum of **4** exhibits two peaks at 8.7 and 9.4 eV which are clearly separated from three peaks between 10 and 11.5 eV. If we assign the third peak (band ⑤) in the PE spectrum of **4** to one transition, the first, second, and fourth peak should correspond to two transitions each, according to their relative intensities. To assign the seven strongly overlapping bands in the PE spectrum of **4** empirically, we compare their positions with those of bicyclo[2.2.2]octadiene (**14**) [17], **5** and bicy-

Table. *Comparison of the Ionization Energies* $I_{v,j}$ *of* **1**–**5** *with Calculated Orbital Energies,* ε_j. All Values in eV.

Compound	Band	$I_{v,j}$	Assignment	$-\varepsilon_j$ (MNDO)	$-\varepsilon_j$ (STO 3G)
1	①	8.06 8.25 8.43	$5a_2$ (π)	8.88	6.39
	②	9.2	$7b_2$ (π)	9.69	7.64
	③	9.35	$14a_1$ (π)	9.77	7.87
	④	9.55	$13a_1$ (σ)	10.79	9.26
	⑤	10.2	$6b_2$ (π)	11.13	10.11
	⑥	10.9	$4a_2$ (σ)	12.28	11.30
	⑦	11.4	$10b_1$ (σ)	12.26	11.39
2	①	8.14	$10b_2$ (π)	9.37	6.83
	②	9.23	$15a_1$ (π)	9.68	7.80
	③	9.4	$9b_2$ (π)	9.74	7.79
	④	9.55	$14a_1$ (π)	10.02	8.19
	⑤	10.1	$13a_1$ (σ)	10.62	9.15
	⑥	11.3	$6a_2$ (σ)	11.17	9.52
	⑦	11.9	$10b_1$ (σ)	12.20	11.24
3	①	8.85	$10b_2$ (π)	9.59	7.35
	②	9.2	$15a_1$ (π)	9.86	7.92
	③	9.65	$14a_1$ (σ)	10.47	8.67
	④	10.1	$7a_2$ (σ)	11.10	9.36
	⑤	10.85	$11b_1$ (σ)	11.57	10.14
4	①	8.7	$10b_2$ (π)	9.50	7.08
	②		$15a_1$ (σ)	9.92	7.80
	③	9.4	$14a_1$ (π)	10.49	8.38
	④		$7a_2$ (σ)	11.04	9.24
	⑤	10.4	$11b_1$ (σ)	11.60	10.25
	⑥	11.0	$9b_2$ (σ)	12.00	10.86
	⑦	11.2	$6a_2$ (σ)	12.22	11.13
5	①	8.7	$15a_1$	10.41	8.11
	②	9.2	$8a_2$	10.93	8.99
	③	9.75	$12b_1$	11.31	9.60
	④	10.6	$9b_2$	11.96	10.73
	⑤	10.8	$7a_2$	12.00	10.74

clo[2.2.0]hexane (**15**) [3] as shown in *Fig. 2*. The comparison of **5** with **15** reveals a large shift of the three σ bands towards lower energy into a region (8.7–9.7 eV) where usually π bands are expected.

Using intensity arguments as mentioned above for the first four peaks in the PE spectrum of **4** and the comparison of these peaks with the first bands in the PE spectra of **5** and **14** (see *Fig. 2*) corroborates that each of the first two peaks in the PE spectrum of **4** is due to two transitions. We notice an especially strong destabilization of $a_1(\sigma)$ by comparing **14** with **4**.

The PE Spectra of 1 and 3. – The first band in the PE spectrum of **1** exhibits distinct vibrational fine structure ($\nu \approx 1500\ \mathrm{cm}^{-1}$). We assign the second feature between 9 and 9.6 eV to three transitions and band ⑤ to one transition. The PE spectrum of **3** shows four close-lying peaks between 8.8 and 10.1 eV, separated from a fourth one at 10.8 eV.

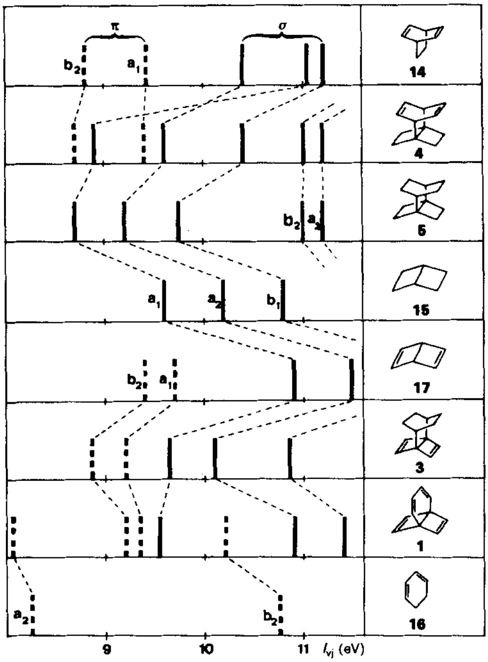


Fig. 2. *Correlation between the first PE bands of* **1**, **3**, **4**, *and* **5** *with those of* **14**–**17**

To assign these peaks empirically, we compare the PE bands of both compounds in *Fig. 2* with the spectra of 1,3-cyclohexadiene (**16**) [18] and *Dewar* benzene (**17**) [3]. This comparison suggests to assign the two peaks at 8.04 and 10.2 eV in the PE spectrum of **1** to $a_2(\pi)$ and $b_2(\pi)$ of the butadiene bridge. The remaining bands can be assigned to the two π-MO's located in the *Dewar* benzene fragment and the three high-lying σ-MO's of the bicyclo[2.2.0]hexane unit encountered in all the other compounds. The stabilization observed for $a_2(\sigma)$ and $b_1(\sigma)$ when comparing the bands of **3** with those of **1** is anticipated since in **1** the destabilizing effect of the ribbon orbitals of the cyclohexane fragment is not present. In line with this argument is the observation that the band corresponding to $a_1(\sigma)$ remains essentially constant in **1** and **3**. The correlation presented in *Fig. 2* gives no evidence for any interaction between $b_2(\pi)$ of the *Dewar*-benzene unit and $b_2(\pi)$ of the 1,3-cyclohexadiene fragment. The spatial overlap of both fragments is essentially zero.

Our PE-spectroscopic investigations on four compounds with the bicyclo[2.2.0]-hexane or the bicyclo[2.2.0]hexadiene skeleton reveal strong dependance of the high-lying σ orbitals upon the substituents while the π-MO's are much less affected.

The PE Spectrum of 2. – The PE spectrum of **2** shows one sharp band at 8.14 eV separated from strongly overlapping bands between 9 and 10.5 eV to which we assign four transitions. From the foregoing discussion, it seems clear that the first peaks of the PE spectrum of **2** are due to ionization from the four possible linear combinations of the π-MO's and the three σ-MO's referred to in the discussion of the PE spectra of **3**–**5**. It seems reasonable to construct the four π-MO's of **2** from the π-MO's of **3** and **4**. To do this, we use a simple ZDO model within a first-order perturbation theoretical approach [19].

To derive the basis orbital energies, we start with the negative values of the ionization energies of the π bands of **3** and **4** (see the *Table*). A comparison of the centers of gravity of the first four bands of **2** (9.08 eV) with that of the first two bands of **3** (9.02 eV) and **4** (9.04 eV) suggests to lower the basis-orbital energies of **3** and **4** by 0.1 eV. This lowering seems reasonable in the light of similar cases [17] [18] where the introduction of additional double bonds in the molecule resulted in a lowering of the basis orbital energies. This yields the following basis orbital energies:

$$\varepsilon\,(b_2(\mathbf{3})) = -8.95 \text{ and } \varepsilon\,(b_2(\mathbf{4})) = -8.8 \text{ eV} \tag{1}$$

$$\varepsilon\,(a_1(\mathbf{3})) = -9.3 \text{ and } \varepsilon\,(a_1(\mathbf{4})) = -9.5 \text{ eV} \tag{2}$$

Similarly, the off-diagonal matrix elements (*i.e.* the orbital interaction terms)

$$\beta\,(b_2) = \langle b_2(\mathbf{3})|\mathcal{H}|b_2(\mathbf{4})\rangle \tag{3}$$

and

$$\beta\,(a_1) = \langle a_1(\mathbf{3})|\mathcal{H}|a_1(\mathbf{4})\rangle \tag{4}$$

can be estimated. The related basis wave functions $a_1(\mathbf{3})$, $a_1(\mathbf{4})$, $b_2(\mathbf{3})$, and $b_2(\mathbf{4})$ correspond to the local AO combinations in the bicyclohexyl (**3**) and cyclohexyl (**4**) moieties of the molecule **2** as

$$b_2(\mathbf{3}) = 1/2\,(p_2 + p_3 - p_5 - p_6) \tag{5}$$

$$b_2(\mathbf{4}) = 1/2\,(p_8 + p_9 - p_{11} - p_{12}) \tag{6}$$

$$a_1(\mathbf{3}) = \frac{1}{\sqrt{6}}(-\sigma_1 + p_2 + p_3 - \sigma_4 + p_5 + p_6) \tag{7}$$

and

$$a_1(\mathbf{4}) = \frac{1}{\sqrt{6}}(-\sigma_7 + p_8 + p_9 - \sigma_{10} + p_{11} + p_{12}) \tag{8}$$

where p_i corresponds to pure $2p_\pi$ atomic orbitals and σ_i to sp^n hybrids localized at the centers i. For simplicity, we assume the coefficients of σ_i and p_j to be the same.

The interaction terms $\beta\,(b_2)$ and $\beta\,(a_1)$ can be chosen to fit the experimental data. This criterium is met by adopting

$$\beta\,(b_2) = -0.3 \text{ eV} \tag{9}$$

and

$$\beta\,(a_1) = -0.5 \text{ eV} \tag{10}$$

as the optimal values for the off diagonal terms defined in *Eqns. 3* and *4*.

Solving the resulting secular determinant leads to a predicted four peak pattern with

$$\varepsilon\,(b_2)\text{: } -8.4 \text{ and } -9.4 \text{ eV}$$

$$\varepsilon\,(a_1)\text{: } -9.1 \text{ and } -9.7 \text{ eV}$$

which is in reasonable agreement to experiment and confirmed by the orbital sequence predicted by the theoretical procedures.

The adopted values given in *Eqns. 9* and *10* can furthermore be justified. Considering the basis wave functions defined above results in a resonance integral $\beta_{\mu\nu}$ of -0.5 eV between two atomic orbitals μ and ν separated by 3 Å. This value has the same order of magnitude as found in compounds with homoconjugation [19] [20] and spiroconjugation [21]. In these compounds, the interacting π systems are separated by 3 to 4 Å, *i.e.* the same order of magnitude as predicted in **2** by MNDO (2.98 Å).

Results of MO Calculations. – The comparison of the calculated orbital energies for **1**–**5** with the ionization energies shows that both methods used predict the σ bands at a too high energy with respect to the π bands. Usually, the reverse is found, *i.e.* the σ bands are predicted at too low energy. This shortcoming could be due to geometrical reasons, *e.g.* the 1,4 distance in the bicyclo[2.2.0]hexane unit is longer than predicted by the calculations. The *Table* shows that the orbital sequence predicted by the MNDO procedure parallels that obtained by our empirical assignment. The split between the π-MO's is underestimated, however. The largest discrepancies are observed for **2**. This inherent shortcoming of the NDO procedures (*i.e.* underestimating spatial interactions) is well-known [22].

The STO 3G results listed in the *Table* reproduce the splitting between the π levels much better, but the first ionization energies are predicted at too low values.

Our MO calculations on **2** reveal a considerable π/σ interaction for the π orbitals $15a_1$ and $14a_1$ of **2**. To analyze the π/σ interaction in **2** in more detail, we apply a procedure suggested by *Heilbronner* and *Schmelzer* [23] to the MNDO results. We observe a strong interaction of the precanonical σ orbitals with the semilocalized π-MO's of a_1 symmetry. The in-phase linear combination of the π-MO's of the bicyclo[2.2.0]hexadiene part and the hexadiene moiety (π_{25}, see *Fig. 3*) interacts strongly with a precanonical σ-MO χ_{24} (see *Fig. 3*), which is mainly localized in the bonds connecting the two ring systems. The corresponding interaction parameter is $\langle \pi_{25} | \mathscr{H} | \chi_{24} \rangle = -2.32$ eV.

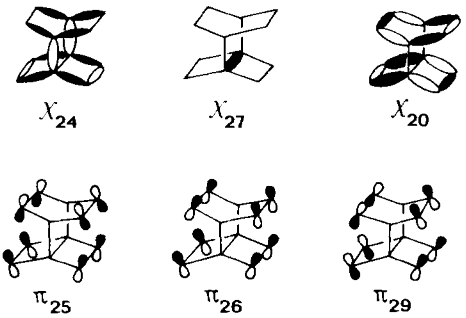


Fig. 3. *Schematic representation of the most important precanonical MO's of* **2** *responsible for the π/σ interaction*

The out-of-phase linear combination of a_1 symmetry (π_{26}, see *Fig. 3*) interacts with a σ-MO strongly localized between the centers 1 and 4 (χ_{27}, see *Fig. 3*). The corresponding interaction parameter is $\langle \pi_{26} | \mathscr{H} | \chi_{27} \rangle = -0.31$ eV. The out-of-phase linear combination of b_2, the HOMO (π_{29}) interacts with the precanonical σ orbital χ_{20} shown in *Fig. 3*: $\langle \pi_{29} | \mathscr{H} | \chi_{20} \rangle = -0.58$ eV, the relative size gives a rough measure of the π/σ interaction prevailing in **2**.

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Experimental. – *General.* M.p. are uncorrected. IR: *Hitachi Model 215* grating spectrometer. NMR: *Hitachi R-24* (60 MHz), *JNM-FX 100* (100 MHz), or a *JNM-FX 200* (200 MHz) spectrometer. Chemical shifts: in ppm, TMS, as internal standard. MS: *JEOL Model JMS-D 300* spectrometer, at 70 eV; ions of each spectrum were normalized to the spectrums most intense ion set equal to 100, relative intensities in parenthesis. PE: *Perkin Elmer PS-18* instrument and on *UPG 200* of *Leybold Heraeus* at r.t. using multiscanning technique by electronic data aquisition with a *Hewlett Packard Computer HP 1000.*

Dibromocarbene Addition to 2,3-Dimethylidenebicyclo[2.2.2]octane (**6**) [7]. A mixture of 6.65 g of **6** [6] (35 mmol), 38 g of $CHBr_3$ (150 mmol), 60 ml of 50% aq. NaOH, 60 ml of CH_2Cl_2, 0.4 g of hexadecyltrimethylammonium bromide, and 0.8 ml of EtOH was stirred at *ca.* 5° for 52 h. The resultant mixture was diluted with 200 ml of benzene/hexane (1:1), washed successively with two portions of H_2O, dil. HCl, aq. $NaHCO_3$, and brine, and dried ($MgSO_4$). After removal of the solvent, the remaining $CHBr_3$ was evaporated under reduced pressure (10^{-2} Torr) without heating. Chromatography of the residual dark-brown oil on silica gel with hexane gave first the mono-adduct closely followed by *2,2,2″,2″-tetrabromodispiro[cyclopropane-1,2′-bicyclo[2.2.2]octane-3′,1″-cyclopropane]* (**7a**). The eluent containing **7a** was concentrated *in vacuo* to give a light-brown oil, which solidified in a refrigerator. Crystallization from hexane gave pure **7a** (6.39 g, 33%), m.p. 127.5–128.5°. ^{1}H-NMR ($CDCl_3$, 100 MHz): 1.3–1.7 (*m*, 2 H); 1.85–2.1 (*m*, 8 H); 2.28 (*d*, *J* = 9.5, 2 H); 2.55–2.85 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 22.87; 24.07; 31.82; 34.93; 36.14; 37.22. Anal. calc. for $C_{12}H_{14}Br_4$: C 30.16, H 2.95, Br 66.89; found: C 30.16, H 2.88, Br 67.09.

Partial Debromination of **7a** *with* Bu_3SnH [8]. To a gently refluxing ethereal soln. of **7a** (6.00 g, 12.6 mmol in 100 ml of dry Et_2O) was added Bu_3SnH (7.60 g, 26.1 mmol) in 50 ml of Et_2O over a period of 1 h. After addition, refluxing was continued for 1.5 h. The resultant mixture was cooled to r.t., washed successively with aq. NaOH and H_2O, and dried ($MgSO_4$). After removal of solvent, the residual oil was chromatographed on silica gel with hexane. The fractions containing the product were combined, concentrated *in vacuo*, and the residual colorless oil was distilled to give 3.47 g of *2,2″-dibromodispiro[cyclopropane-1,2′-bicyclo[2.2.2]octane-3′,1″-cyclopropane]* (**7b**; 86%), b.p. 85–95°/4 × 10^{-3} Torr. The GLC and spectroscopic analysis of the distillate showed that it mainly consisted of two isomeric products. The mixture was used for the subsequent reaction without separating the components. The ^{1}H-NMR ($CDCl_3$): major component: 0.96 (br. *s*, 2 H); 1.1–2.0 (*m*, 12 H); 2.85 (*q*, *J* = 5.5, 8.2, 2 H).

Dehydrobromination of **7b** [5]. To 2.45 g of **7b** (7.7 mmol) in 35 ml of dry pentane was added 40 ml of a 0.61M DMSO soln. of *t*-BuOK over a period of 40 min. After 1 h at r.t., additional 30 ml of the DMSO soln. of *t*-BuOK was added. After stirring for 1 h, the mixture was poured into 250 ml of ice water and the aq. soln. was extracted with two portions of pentane. The pentane solns. were combined, washed successively with two portions of H_2O and brine, and dried (Na_2SO_4). After removal of the solvent, the residual oil was subjected to chromatography on silica gel. Elution with pentane successively afforded *bispiro[cycloprop-2-ene-1,2′-bicyclo[2.2.2]octane-3′,1″-cycloprop-2″-ene]* (**8**), the monodehydrobrominated product, and 2-ethynyl-3-vinylbicyclo[2.2.2]oct-2-ene. The ^{1}H-NMR ($CDCl_3$, 100 MHz) of **8**: 0.93 (*m*, 2 H); 1.5–2.0 (*m*, 8 H); 7.09 (*s*, 4 H).

Compound **8** was subjected to Ag^+-promoted rearrangement [5] without further purification because of its instability.

2,5-Ethano[4.2.2]propella-7,9-diene (**3**). Compound **8**, which was obtained from 2.45 g of **7b**, was dissolved in 20 ml of $MeNO_2$. To the soln., cooled in an ice bath, was added 10 mg of $AgClO_4$. After 20 min, **8** had been consumed. The mixture was poured into pentane, washed with aq. NaOH and H_2O, and dried ($MgSO_4$). The GLC analysis showed that the reaction cleanly afforded two products in a ratio of *ca.* 1:1. The two products were separated by chromatography on silica gel with pentane. Spectroscopic analysis showed that they were **3** and *1,2,3,4-tetrahydro-1,4-ethanonaphthalene* (**9**)^1). Compound **3** was further purified by prep. GLC to give 102 mg of **3** (8.4% from **7b**), m.p. 175.5°–176.5° (in a sealed tube). ^{1}H-NMR ($CDCl_3$, 100 MHz): 1.3–1.8 (sym. *m*, 8 H); 2.24 (br. *s*, 2 H); 6.58 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$): 23.01; 33.41; 59.85; 145.07. MS: 158 (12, M^+), 30 (65), 129 (100), 128 (31), 127 (10), 115 (46), 91 (10), 77 (11), 51 (13). Anal. calc. for $C_{12}H_{14}$: C 91.08, H 8.92; found: C 90.86, H 8.85.

2,5-Ethano[4.2.2]propellane (**5**). Catalytic hydrogenation of **3** over Pt black was carried out in EtOH. The resultant product was purified by prep. GLC; m.p. 224°–225.5° (in a sealed tube). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.35 (br. *s*, 2 H); 1.47 (*m*, 4 H); 1.94 (*m*, 4 H); 2.10 (*m*, 4 H); 2.10 (*m*, 4 H); 2.46 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 22.52; 28.47; 40.01. MS: 162 (52, M^+), 147 (20), 134 (36), 133 (33), 119 (45), 106 (53), 105 (55), 93 (63), 92 (30), 91 (77), 80 (36), 79 (100). Anal. calc. for $C_{12}H_{18}$: C 88.82, H 11.18; found: C 88.71, H 11.33.

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^{1}) In MeCN, the ratio **3**/**9** was *ca.* 1:2. In MeOH, the ratio **3**/**9** was found to be *ca.* 2:1, but a substantial amount of MeOH adduct was formed concurrently.

Bicyclo[2.2.0]hexane-1,4-dimethyl Bis(methanesulfonate) (**11b**). *Bicyclo[2.2.0]hexane-1,4-dimethanol* (**11a**) was obtained by $LiAlH_4$ reduction of *dimethyl bicyclo[2.2.0]hexane-1,4-dicarboxylate* (**10**) [9]. To a CH_2Cl_2 soln. (150 ml) of **11a** (2.61 g, 18.4 mmol) and Et_3N (5.46 g, 54 mmol) cooled in an ice-MeOH bath was added 5.0 g of MsCl (43.6 mmol) over a period of 20 min at –20° [24]. After addition, the resultant suspension was stirred for 1.5 h while the temp. of the mixture was allowed to rise to 0°. The mixture was washed successively with dil. HCl, H_2O, and aq. $NaHCO_3$, and dried ($MgSO_4$). After removal of the solvent, the residue was crystallized from CH_2Cl_2/Et_2O to give 4.2 g of **11b** (77%), m.p. 107.5–108°. IR (KBr): 1350, 1340, 1325, 1280, 1270, 990, 975, 955, 940, 925, 840, 830. ^1H-NMR ($CDCl_3$, 100 MHz): 2.0–2.4 (sym. *m*, 8 H); 3.05 (*s*, 6 H); 4.20 (*s*, 4 H). Anal. calc. for $C_{10}H_{18}S_2O_6$: C 40.26, H 6.08, S 21.50; found: C 40.09, H 6.10, S 21.42.

Bicyclo[2.2.0]hexane-1,4-bis(acetonitrile) (**11c**). A mixture of 4.0 g of **11b** (13.4 mmol) and 2.0 g of NaCN (40.8 mmol) in 50 ml of DMF was stirred for 3 h at r.t. The resultant mixture was poured into 200 ml of H_2O and the product was extracted with 4 × 100 ml of Et_2O. The ethereal extracts were combined, washed twice with H_2O, and dried ($MgSO_4$). After removal of the solvent, the residue was distilled to give 1.63 g of **11c** (76%), b.p. 90–95°/4.5 × 10^{-3} Torr. ^1H-NMR ($CDCl_3$, 100 MHz): 2.28 (*s*, 8 H); 2.59 (*s*, 4 H). IR (KBr): 2980, 2950, 2860, 2250, 1440, 1420. MS: 160 (1.4, M^+), 120 (20), 93 (58), 91 (21), 80 (38), 79 (62), 53 (100). Anal. calc. for $C_{10}H_{12}N_2$: C 74.96, H 7.55, N 17.49; found: C 75.06, H 7.32, N 17.62.

Bicyclo[2.2.0]hexane-1,4-bis(acetaldehyde) (**11d**). A toluene soln. (3 ml) of **11c** (100 mg, 0.62 mmol) was treated with 0.46 ml of 50% $(i\text{-}Bu)_2AlH$ in hexane at –50°. The mixture was slowly warmed up to 0° and stood overnight at this temp. The mixture was added dropwise to a stirred mixture of 10 ml of Et_2O and 5 ml of 5% H_2SO_4. The aq. layer was saturated with NaCl, and the hydrolyzed product was extracted with two portions of Et_2O. The ethereal extracts were combined, washed twice with brine, and dried (Na_2SO_4). Yield of the crude product was 60 mg. GLC showed that a small amount of **11c** remained. Distillation of the crude product gave 45 mg of **11d** (43%), b.p. 60°/4 × 10^{-3} Torr. IR (neat): 2940, 2860, 2730, 1720. ^1H-NMR ($CDCl_3$, 60 MHz): 2.16 (*s*, 8 H); 2.53 (*d*, *J* = 2, 4 H); 9.65 (*t*, *J* = 2, 2 H).

[4.2.2]Propell-3-ene (**12**). To 2.39 g of $LiAlH_4/TiCl_3$ (1:2) mixture cooled in an ice bath was added 100 ml of THF under Ar and the mixture was stirred at 0° for 30 min and then refluxed for 1.5 h [10]. A soln. of 0.40 g of **11d** (2.4 mmol) in 5 ml of THF was added from a hypodermic syringe over a period of 4 h. After refluxing overnight, the dark suspension was treated with 40 ml of 2N HCl and extracted with two portions of pentane. The extracts were combined, washed twice with H_2O, and dried ($MgSO_4$). After removal of the solvent through a 15-cm packed column, the residue was chromatographed on silica gel with pentane. The pentane was evaporated through a 10-cm *Vigreux* column, and the residue was subjected to prep. GLC to give 30 mg of **12** (9.3%). ^1H-NMR ($CDCl_3$, 60 MHz): 1.8–2.2 (*m*, 12 H); 5.80 (*s*, 2 H).

[4.2.2]Propella-3,5-diene (**13**). To a soln. of 52 mg of **12** (0.39 mmol) in 3 ml of CH_2Cl_2 were added 0.1 ml of pyridine and 130 mg of pyridinium-bromide-perbromide (0.41 mmol). Within 30 min at r.t., the soln. became pale yellow. GLC of the mixture showed that **12** had largely been consumed. The mixture was diluted with CH_2Cl_2, washed successively with dil. HCl, aq. $Na_2S_2O_3$, and H_2O, and dried ($MgSO_4$). After removal of the solvent, 108 mg of an oil was obtained.

The crude dibromide was dissolved in 3 ml of HMPA and added to a mixture of 200 mg of Li_2CO_3 and 100 mg of LiCl which had been dried at 140°/2 Torr for 1 h [25]. The suspension was stirred at 90° for 3 h. After cooling to r.t., the mixture was poured into 10 ml of H_2O and extracted with two portions of pentane. The extracts were combined, washed well with H_2O, and dried ($MgSO_4$). The solvent was removed through a 10-cm *Vigreux* column, and the residue was subjected to prep. GLC to give 38 mg of **13** (72%). ^1H-NMR (C_6D_6, 60 MHz): 2.15–2.80 (*AA'BB'*, *m*, 8 H); 5.35–5.85 (*AA'BB'*, *m*, 4 H).

2,5-Etheno[4.2.2]propell-3-ene (**4**). A soln. of 35 mg of **13** (0.26 mmol) and 100 mg of maleic anhydride (1.0 mmol) in 2.0 ml of benzene was placed in a glass ampoule and heated at 110° for 22 h. GLC showed a single product peak besides those of remaining maleic anhydride and a trace amount of **13**. After removal of the solvent, the flask containing the crystalline residue was evacuated to 10^{-2} Torr to remove the unreacted maleic anhydride. The NMR spectrum of the crude crystalline product (63 mg) was consistent with the structure of the expected *Diels-Alder* adduct.

The above product and 250 mg of $Ni(CO)_2(Ph_3P)_2$ (0.39 mmol) were dissolved in 4 ml of diglyme and the mixture was vigorously refluxed for 45 min [11]. The mixture was poured into a mixture of pentane/H_2O and the org. layer separated was washed well with H_2O. GLC showed a single major product peak. After removal of the solvent through a 10-cm *Vigreux* column, the residue was chromatographed on silica gel with pentane. The product **4** was isolated by prep. GLC (20 mg, 48%) and further purified by sublimation at 80–85°. ^1H-NMR ($CDCl_3$, 60 MHz): 1.35–2.15 (*AA'BB'*, *m*, 8 H); 3.44 (*m*, 2 H); 6.40 (*m*, 4 H). MS: 158 (34, M^+), 143 (97), 142 (22), 130 (57), 129 (100), 128 (85), 117 (32), 115 (61), 104 (27), 91 (66), 79 (31), 78 (31), 77 (33). *m/z* of M^+ = 158.1130 (calc. for $C_{12}H_{14}$: *m/z* = 158.1096).

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