dried ($MgSO_4$) extract was concentrated by fractionation. Purification of the residue by vacuum distillation and thin-layer chromatography (silica gel, pentane) gave 0.4 g (83% yield) of alkylation product **2** which was shown to be 96.5% cis isomer by hydrogenation followed by GC analysis of the resulting saturated analogue **4**. The spectral properties of the alkylation product obtained in this experiment were indistinguishable from those for authentic *cis*-**2** described above.

The other experiments summarized below eq 1 were carried out in a similar manner. The alkylation product derived from *cis*-1-OPiv had the same spectral properties as an authentic sample of *trans*-**2**.

Alkylation of (*R*)-(+)-α-Methyl-γ-phenylallyl Pivalate (*R*-(+)-5-OPiv) with *n*-BuMgBr Containing 1 Mole % CuCN or CuCl. These procedures were the same as reported earlier for alkylation of racemic 5-OPiv.[1]

The product obtained by alkylation with *n*-BuMgBr containing 1% CuCl was isolated in 96% yield, and the composition was determined by capillary GC (94 ft, UCON LB-550X, 130 °C). A portion of this product was converted to 2-methylhexanoic acid (**8**) by Lemieux oxidation using a procedure reported earlier for this same transformation.[12] A pure sample of **8** had $[\alpha]^{22}_D$ −20.09° (*c* 6.02, ether). From the absolute configuration and rotation for this compound,[12] it can be seen that this product had the *R* configuration and an ee of 92%. The spectral properties were the same as for an authentic sample of (*dl*)-**8**.[12]

A portion of the same alkylation product was reduced with diimide by a standard procedure published earlier for a similar transformation.[5] The reduction product was isolated in 91% yield and a homogeneous sample of 3-methyl-1-phenylheptane (**9**) was obtained by preparative GC (10 ft, UCON LB-550X on Chromosorb P, 130 °C). This material had the same spectral properties and capillary GC retention time as the authentic racemic sample described above. A homogeneous sample of **9** derived from the alkylation product had $[\alpha]^{25}_D$ −8.55° (*c* 3.58, *n*-hexane). This has the same configuration and ee as the (*R*)-(−)-**8** obtained from the same alkylation product. Thus (−)-**9** has the *R* configuration and the absolute rotation is $[\alpha]^{25}_D$ 9.3° (*n*-hexane). The results for alkylation of (*R*)-(+)-5-OPiv with *n*-BuMgBr containing 1 mol % CuCl are presented in Scheme I.

The product obtained by alkylation with *n*-BuMgBr containing 1% CuCN was isolated in "quantitative" yield. The composition was determined by capillary GC (94 ft, LB-550X, 130 °C) and (299 ft, QF-1, 130 °C). The latter column is effective for resolution of (*E*)- and (*Z*)-**7**.

Diimide reduction of this product by the procedure used earlier for this same transformation,[5] followed by purification by preparative GC (10 ft, UCON LB-550X on Chromosorb P, 130 °C), gave a homogeneous sample of **10**, $[\alpha]^{25}_D$ −5.40° (*c* 5.78, hexane). From the absolute configuration and rotation for this compound[5] it can be seen that this sample had the *R* configuration and an ee of 63%. The spectral properties and capillary GC retention time were the same as for an authentic sample.[5]

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Electronic Structure of Octavalene. Photoelectron Spectroscopic Investigations†

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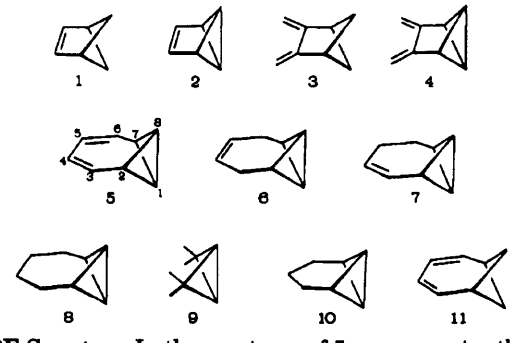
The He I photoelectron (PE) spectra of octavalene (**5**) as well as its hydrogenated products **6–8** have been investigated. The assignment given is based on an empirical comparison of **5–8** with related compounds, a ZDO model, and semiempirical and ab initio calculations. Within the ZDO model the interaction between the butadiene moiety and the bicyclobutane fragment of **5** is described by a resonance integral of −2.3 eV. The orbital sequence of **5** is found to be $2a_2$ ($\pi - \sigma$), $9a_1$ (σ), $3b_1$ ($\pi - \sigma$), $1a_2$ ($\sigma + \pi$), $2b_1$ ($\sigma + \pi$).

The comparison between bicyclo[2.1.1]hexene (**1**) and benzvalene (**2**) as well as 2,3-bis(methylene)bicyclo[2.1.1]hexane (**3**) and 3,4-bis(methylene)tricyclo[3.1.0.0^{2,6}]hexane (**4**) reveals a stronger interaction between the π fragment and the bicyclobutane moiety compared to the four-membered-ring fragment.[1] Using data from photoelectron (PE) spectroscopic investigations yields a resonance integral β of −1.9 eV for **1** and **3** and −2.3 eV for **2** and **4**.

The recent synthesis of octavalene (**5**)[2] and its hydrogenated congeners **6–8**[2c] allows us to explore the electronic structure of **5–8** and to check the above-mentioned interaction parameters.

In the following we will report on the He I PE data of **5–8**. In Figure 1 we show the PE spectra of **5–8** and in Table I we list the recorded vertical ionization energies, $I_{v,j}$.



PE Spectra. In the spectrum of **5** we encounter three bands below 11 eV. The first and third show a relatively steep onset while the second is more Gaussian like. In the PE spectrum of **6** we see two peaks below 12 eV. The

† Dedicated to Professor Heinz A. Staab on the occasion of his 60th birthday.

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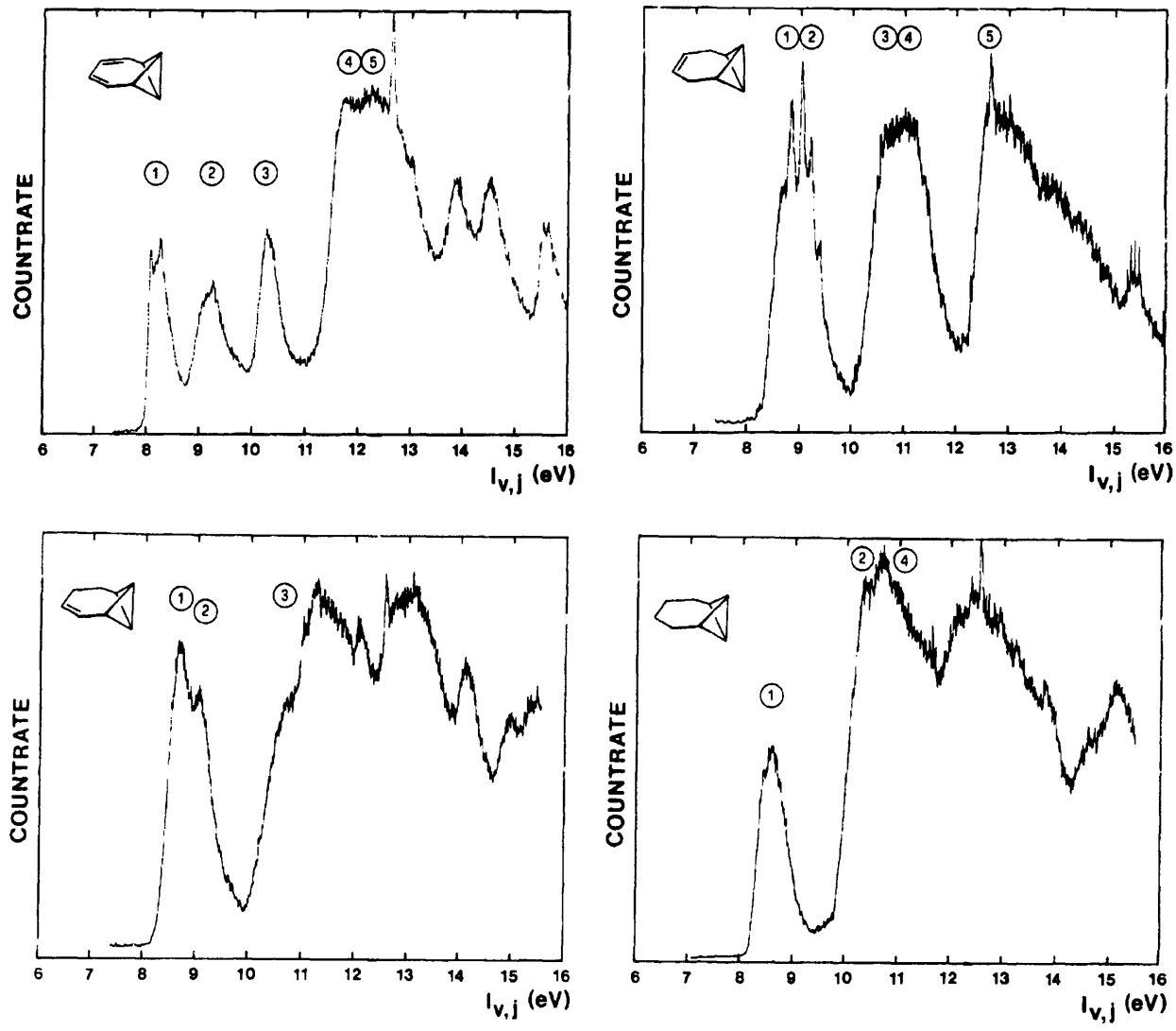

Figure 1. He I PE spectra of 5–8.

Table I. Comparison between the Recorded Vertical Ionization Energies ($I_{v,j}$) of 5–8 and the Calculated Orbital Energies

compd	band	$I_{v,j}$	assignment	−ε(ZDO)	−ε(MNDO)	−ε(STO 3G)
5	1	8.09 8.28	$2a_2(\pi - \sigma)$	7.9	8.82	6.23
	2	9.25	$9a_1(\sigma)$	9.3	10.18	8.22
	3	10.25	$3b_1(\pi - \sigma)$	10.3	10.74	9.31
	4	11.72	$1a_2(\sigma + \pi)$	11.9	12.27	11.46
	5	12.2	$2b_1(\sigma + \pi)$	12.0	12.49	12.01
6	1	8.81	$11a(\sigma)$		9.99	7.90
	2	9.03 9.30	$10b(\pi)$		9.69	7.62
	3	10.7	$10a(\sigma)$		11.40	9.98
	4	11.1	$9b(\sigma)$		11.47	10.27
7	1	8.7	π		9.57	6.61
	2	9.1	σ		10.10	7.96
	3	10.7	σ		11.31	9.68
8	1	8.6	12a		9.95	7.72
	2	10.45	11a		11.19	9.48
	3	10.7	10b		11.35	9.97
	4	11.0	6b		11.78	10.51

appearance of the first band is indicative of two superimposed bands, one broad Gaussian type and a steep one with vibrational fine structure. If we use the area of the bands to judge the number of transitions we also conclude two transitions for the second peak in the PE spectrum of 6. The PE spectrum of 7 shows two strongly overlapping bands at 8.7 and 9.1 eV well separated from a shoulder at 10.7 eV. The PE spectrum of 8 shows one band at 8.6

Table II. Calculated Distances (Å) and Heats of Formation (kcal/mol) of 5–8 according to the MNDO Procedure

compd	ΔH_f	C(1)–C(2)	C(2)–C(3)	C(3)–C(4)	C(4)–C(5)	C(1)–C(8)	C(2)–C(7)
5	95.92	1.54	1.48	1.35	1.46	1.52	2.36
6	74.19	1.53	1.52	1.50	1.34	1.54	2.36
7	73.51	1.54	1.48	1.35	1.50	1.52	2.35
8	57.75	1.53	1.51	1.54	1.54	1.54	2.35

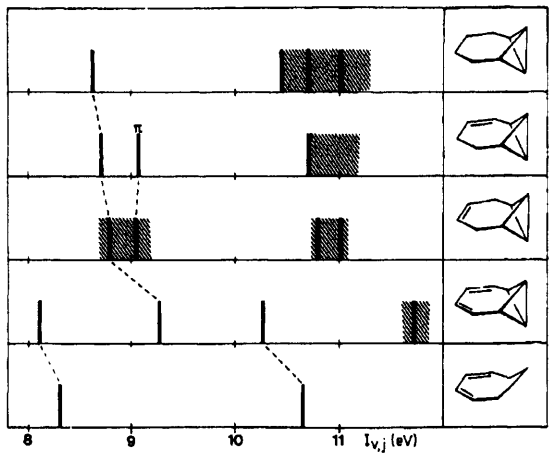

Figure 2. Comparison between the first bands of the PE spectra of 5–8 and cyclohepta-1,3-diene.

separated by about 2 eV from a broad peak.

Interpretation. To interpret the PE spectra we proceed in two ways: Empirically by comparing them with spectra of related species and also by comparing the measured vertical ionization energies with orbital energies derived from several calculation procedures. In both cases we assume that the MO picture valid for the ground state is also useful for the different ionic states. This means that we can set equal the measured vertical ionization energies ($I_{v,j}$) to the calculated orbital energies ($-\epsilon_j$) (Koopmans' approximation).[3]

We start our interpretation by comparing the PE spectrum of 8 with that of simple substituted bicyclobutane derivatives like 2,4-tetramethylbicyclobutane (9)[4] and tricyclo[4.1.0.0^{2,7}]heptane (10).[4,5] Both compounds show one band between 8.6 and 8.8 eV, followed by three close-lying bands between 10 and 11 eV. The first band has been assigned to ionizations from the a_1 MO, the three other bands to ionizations from a_2, b_2, and b_1. This comparison suggests assigning band 1 in the PE spectrum of 8 to a_1 and bands 2–4 to a_2, b_2, and b_1.

In the PE spectra of 6 and 7 we expect one additional band in the low energy region due to the ionization from the π MO. This is indeed the case. In Figure 2 we have compared the first bands of the PE spectra of 5–8. The comparison of the spectra of 6–8 suggests an assignment of the first band of all three spectra to the ionization from the a_1 MO. This also seems reasonable since this MO should be unaffected by the side chain due to its strong localization in the 1,3 σ bond.[4] The comparison between the spectrum of 5 with that of 8 suggests an assignment of the second peak in the PE spectrum of 5 to the a_1 MO. Comparing of the PE spectrum of 5 with the PE data of 1,3-cycloheptadiene[6] suggests assigning band 1 of 5 to ionizations from the $a_2(\pi)$ MO while band 3 is due to ejection of electrons from $b_1(\pi)$ (see Figure 2).

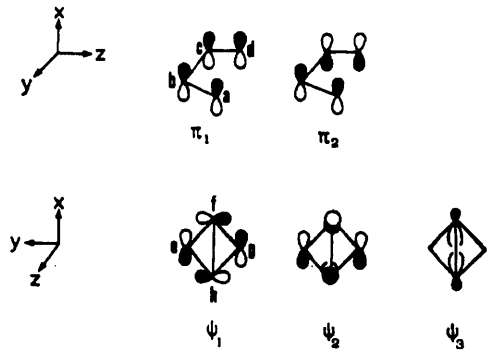

Figure 3. Schematic representation of the fragment MOs of the butadiene unit and the bicyclobutane moiety.

Calculations. Since the geometries of 5–8 are unknown we have optimized their heat of formation (ΔH_f) with respect to their geometrical parameters using the MNDO procedure. The most relevant distances are listed in Table II together with the calculated values for the heats of formation. The MNDO method predicts for 6–8 that the carbon atoms 3–6 are essentially in one plane. This result is unexpected but probably due to the method, which is known to underestimate puckering amplitudes. As a result of this shortcoming, the C(2)–C(7) distance is nearly the same for all four compounds.

The geometrical parameters obtained by the MNDO method were used to carry out ab initio calculation using a minimal basis (STO 3G)[8] on 5–8. The orbital energies obtained are listed in Table I. The sequence predicted by the ab initio approach parallels that of the semiempirical method. As usual, the STO 3G basis gives ionization energies which are too low.

In the case of 6 both procedures predict as HOMO the π MO 10b followed by 11a, the σ MO localized strongly in the central bond of the bicyclobutane moiety.

ZDO Model. Using perturbation theory[9] we can derive the valence MO's of 5 from a butadiene fragment and a bicyclobutane moiety. To do this in a semiquantitative way, we have to define the wave functions and basis orbital energies of the fragment MOs. The wave functions for the two fragments of 5 are the well-known HMOs of butadiene and the valence MOs of bicyclobutane. These wave functions together with their irreducible representations in the point group C_{2v} are

$$\pi_1(b_1) = 0.372(p_{xa} + p_{xd}) + 0.602(p_{xb} + p_{xc}) \quad (1)$$

$$\pi_2(a_2) = 0.602(p_{xa} - p_{xd}) + 0.372(p_{xb} - p_{xc}) \quad (2)$$

$$\Psi_1(a_2) = -0.5(p_{yh} - p_{xe} - p_{yf} + p_{xg}) \quad (3)$$

$$\Psi_2(b_1) = 0.5(\phi_{zh} - p_{xe} - \phi_{zf} - p_{xg}) \quad (4)$$

$$\Psi_3(a_1) = 1/2^{1/2}(\phi_{xf} - \phi_{xh}) \quad (5)$$

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In (1)–(5) the $p_{\mu i}$'s are pure p_π atomic orbitals, while the $\phi_{\mu i}$'s are sp^n_μ hybrid atomic orbitals roughly parallel to the μ axis. For Ψ_1 and Ψ_2 we have assumed that the coefficients at all four positions are about equal in magnitude. This assumption is in line with the results of semiempirical and ab initio calculations on bicyclobutane.[10] A schematical representation of the fragment MOs is given in Figure 3.

For the orbital energies of the butadiene fragment we use the same values as in the case of bicyclo[4.1.1]octa-2,4-diene (11).[11] To assess the basis orbital energies of

$$\epsilon(\pi_2) = -8.4 \text{ eV}$$

$$\epsilon(\pi_1) = -10.9 \text{ eV}$$

the four highest occupied MOs of the bicyclobutane unit we have to keep in mind their strong dependence on the dihedral angle θ between the two three-membered ring fragments of the bicyclobutane moiety.[1,5] Our MNDO calculations on 5 suggest a θ value of 124°. This rather small value might be either due to the method used or due to an enlargement of the angles at atoms 2 to 7. The value predicted for 5 is close to the experimental value reported for bicyclobutane (121.7°);[12] therefore we use the ionization energies of bicyclobutane[4,13] as starting point for our estimation. We previously estimated the inductive effect of the butadiene bridge[11] as 0.2 eV. This yields the following orbital energies:

$$\epsilon(a_1) = -9.14 - 0.2 \text{ eV} = -9.34 \text{ eV}$$

$$\epsilon(a_2) = -11.23 - 0.2 \text{ eV} = -11.43 \text{ eV}$$

Assuming that at dihedral angles around 125° the orbital energies of a_2 and b_1 of the bicyclobutane fragment are nearly equal,[1,5] we estimate for $\epsilon(b_1) = -11.4$ eV. To describe the interaction with the butadiene fragment we use the same value for the resonance integral (−2.3 eV) between the two fragments as for 2 and 4.[1] By solving the corresponding secular equations we obtain the values listed in Table I. The results of the ZDO calculations are summarized in Figure 4. In this figure we show on the left side the occupied π MOs of the butadiene unit and on the right side the valence MOs of the bicyclobutane fragment of 5. The resulting orbital energies, given in the middle, are taken from the ZDO calculations. The wave functions are drawn schematically. The interaction diagram in Figure 4 nicely demonstrates that 5 is an ideal molecule to study the interaction between a butadiene unit and a bicyclobutane fragment.

The orbital energies obtained by our ZDO approach compare well with the measured bands 1 and 3–5. The chosen basis orbital energy for a_1 ($\epsilon = -9.3$ eV) corresponds very well to band 2. The vibrational fine structure observed for band 1 (0.19 eV) is the same as for the first band in 11.

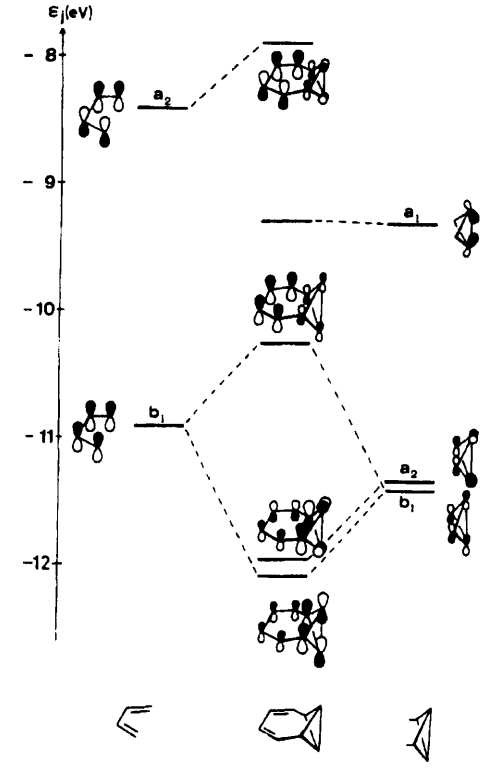

Figure 4. Orbital interaction diagram for 5 based upon perturbation theory.

Conclusion. One aim of our study has been to elucidate the orbital sequence of the highest occupied MOs of 5. This has been accomplished by comparing the first bands of the PE spectrum of 5 with related species and by carrying out MO calculations of different level of sophistication.

Another aim was to check the interaction parameter β derived for 2 and 4. The comparison between 11 and 5 shows that the interaction between the bicyclobutane moiety and the butadiene fragment is considerably stronger than the interaction between a cyclobutane ring and the butadiene in 11.

Experimental Section

The PE spectra of 5–8 have been recorded on a Perkin-Elmer PS-18 instrument and on a UPG 200 of Leybold Heraeus at room temperature by using multiscanning techniques by electronic data acquisition with a Hewlett Packard Computer HP 1000. Both spectrometers gave identical spectra. The spectra shown in Figure 1 result from the PS 18 instrument. The synthesis of 5 admixed with cyclooctatetraene has been reported in the literature.[2a,b] The syntheses of pure 5 and of 6–8 will be described soon.[2c] Compound 8 was contaminated with about 11% bicyclo[5.1.0]oct-2-ene.[2c]

Registry No. 5, 35438-35-8; 6, 102575-25-7; 7, 102575-26-8; 8, 36328-29-7.

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