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Electronic Structure of the Tricyclo[2.1.0.0^{2,5}]pentane System. Photoelectron Spectroscopic Investigations of 1,5-Dimethyl-3-*exo*-methylenetricyclo[2.1.0.0^{2,5}]pentane and 1,5-Dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one

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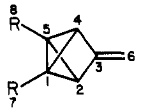
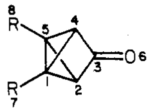
The He(I) photoelectron spectra of 1 and 2 have been recorded. The first bands of their spectra have been assigned to ionizations from molecular orbitals localized at the bicyclobutane fragment (a_1) followed respectively by the π and the 2p lone-pair orbitals of the oxygen atom. This analysis is based on MINDO/3 calculations. It is suggested that electrophiles attack 1 at the bicyclobutane moiety and that the acceptor property of the CO group contributes to the relatively short bond length of the 1,5 bond in 2.

The bicyclobutane moiety shows several interesting aspects: (1) the strong ability to interact with adjacent π systems as exemplified by several spectroscopic investigations,[1-4] (2) a strong variation of the MO levels as a function of the dihedral angle,[1,2a] and (3) a strong variation of the central C–C bond with variation in this angle.[5]

To contribute to the first topic, we have studied the He(I) photoelectron (PE) spectra of 1,5-dimethyl-3-*exo*-methylenetricyclo[2.1.0.0^{2,5}]pentane (1) and 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one (2).



1, R = CH_3
3, R = H



2, R = CH_3
4, R = H

PE Spectrum of 1

The PE spectrum of 1 is shown in Figure 1. It shows one broad peak centered around 9 eV consisting of three strongly overlapping bands (bands 1–3) well separated from a single peak at 11.1 eV. To interprete these results, we assume the validity of Koopmans' theorem ($-\epsilon_J = I_{V,J}$)[6] which allows us to compare the measured ionization energies, $I_{V,J}$, with the calculated orbital energies, $-\epsilon_J$, for the ground state of the closed-shell molecule.

To derive the orbital energies, we use the MINDO/3 method[7] which proved to be quite reliable for hydrocarbons concerning their geometrical parameters and the sequence of orbitals. The calculation predicts for 1 three close lying orbitals ($9a_1$, $5b_2$, and $2a_2$) followed by a fourth one ($5b_1$; see Table I). To understand this sequence qualitatively, we start out with the highest occupied orbitals of tricyclo[2.1.0.0^{2,5}]pentane (5). These orbitals can be derived from those of a hypothetical bicyclobutane[1] with a dihedral angle of 90° and the valence orbitals of a CH_2 group. In Figure 2 we have shown schematically the highest occupied MO's of 5 in the center. Replacing the geminal hydrogens at the 3-position by a carbon/carbon double bond will yield 3-*exo*-methylenetricyclo[2.1.0.0^{2,5}]pentane (3). This will leave $6a_1$, $1a_2$, and $3b_1$ of 5 essentially unchanged. For reasons of symmetry the π orbital of the double bond interacts with $3b_2$ of 5, yielding a high-lying π level ($3b_2$) as shown on the left of Figure 2. In 1 the two methyl groups at the 1- and 5-positions will destabilize the a_1 orbital more than the b_2, giving rise to the orbital sequence reported in Table I.

Table I. Comparison between the Measured Ionization Energies, $I_{V,J}$, of 1 and 2 with the Calculated Orbital Energies, ϵ_J

compd	band	$I_{V,J}$, eV	assignment	$-\epsilon_J$, eV
1	1	8.54	$9a_1(\sigma)$	8.50
	2	8.96	$5b_2(\pi)$	8.77
	3	9.53	$2a_2(\sigma)$	9.13
	4	11.1	$5b_1(\sigma)$	9.87
2	1	9.38	$9a_1(\sigma)$	8.90
	2	9.6	$5b_1(\pi)$	9.27
	3	10.1	$2a_2(\sigma)$	9.62
	4	11.17	$5b_2(\sigma)$	10.53

Our assignment of the orbital sequence in 1 is supported by a comparison between the first PE bands of 1 and those of benzvalene (see Figure 3). If we assume that the methyl groups in 1 destabilize the high-lying σ orbitals of the bicyclobutane fragment (a_1, a_2, b_1, and b_2)[1,2a] by about the same amount, we come to the conclusion that the first band in 1 should be due to the ionization out of $9a_1$ (σ). The higher ionization potential of $5b_2$ in 1 as compared with $4b_2$ in benzvalene can be explained by the different $3b_2$ basis orbital energies (see Figure 2) of the bicyclo-

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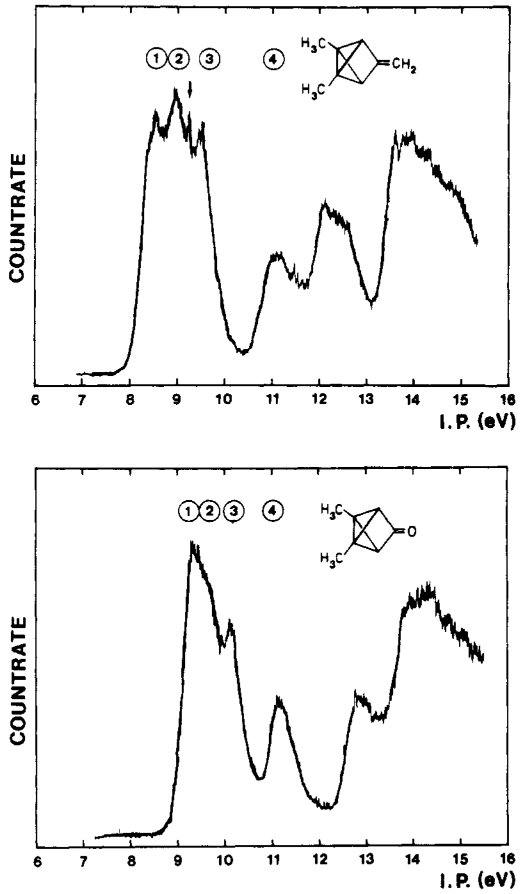

Figure 1. He(I) PE spectra of 1 and 2. The arrow marks a trace of benzene.

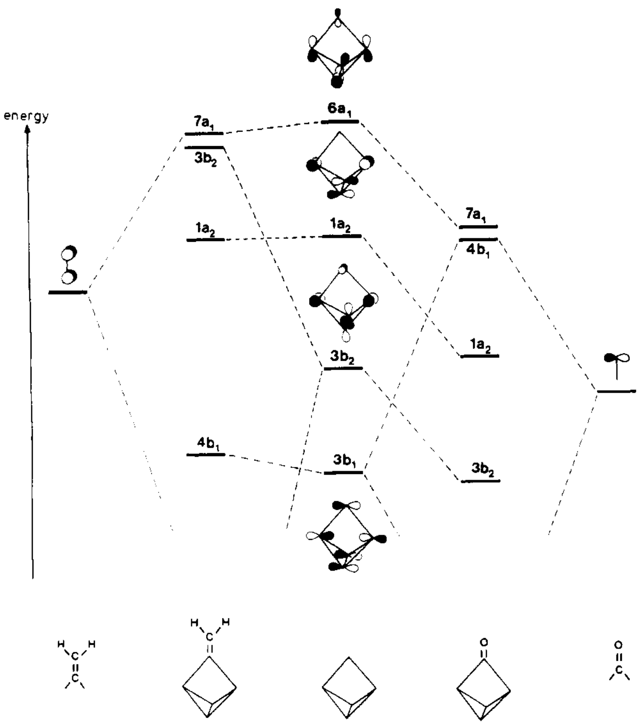

Figure 2. Qualitative correlation diagram between the highest occupied MO's of tricyclo[2.1.0.$0^{2,5}$]pentane (5) and a double bond to yield 3 (left) and a 2p orbital on oxygen to yield 4 (right).

butane fragments. Recently it has been shown that the valence orbitals of the bicyclobutane moiety depend strongly on the dihedral angle:[1] As the dihedral angle θ becomes smaller (benzvalene, 105°; 1, 93°), the orbital energy of $3b_2$ increases, and thus the interaction with the higher lying π orbital is mitigated (see Figure 2).

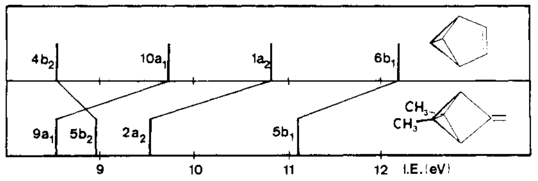

Figure 3. Comparison between the first bands in the PE spectrum of benzvalene and 1.

Table II. Calculated (MINDO/3) Distances for 1 to 4

atoms[a]	distance, pm 1	2	3	4
C_1-C_2	155.3	155.6	154.0	154.2
C_2-C_3	152.5	152.2	152.9	152.7
C_1-C_5	150.9	150.0	147.3	146.6
C_3-C_6	132.8		138.2	
C_3-O_6		119.4		119.4
C_1-C_7	146.8	146.9		

[a] Angle θ: 1, 91°; 2, 93°; 3, 93°; 4, 95°.

PE Spectrum of 2

The PE spectrum of 2 (Figure 1) is very similar to that of 1 as far as it exhibits a broad first peak with three strongly overlapping bands (bands 1–3) followed by a single peak (band 4). From Table I we see that MINDO/3 predicts three MO's ($9a_1$, $5b_1$, and $2a_2$) well separated from $5b_2$. To understand this sequence, we start again with the highest occupied MO's of 5 (Figure 2, center). Replacing formally the geminal H atoms of 5 by an oxygen atom will yield tricyclo[2.1.0.$0^{2,5}$]pentan-3-one (4). The introduction of the oxygen has two effects: an inductive effect which lowers all levels and a conjugative effect due to the interaction with the 2p lone pair at the oxygen. For reasons of symmetry the 2p lone pair interacts with $3b_1$ only, giving rise to a low-lying $4b_1$ orbital in 4. This interaction is indicated on the right side of Figure 2.

As in the case of 1, the two methyl groups at the bridgehead positions in 2 will destabilize the HOMO (a_1) of 4 more than the b_1 level, leading to the orbital pattern shown in Table I.

Final Remarks

Our investigations confirm that the MINDO/3 method is very useful in predicting the orbital sequence in the strained systems 1 and 2.

Recently a relatively short 1,5-bond length in 2 (1.417 Å) and derivatives thereof has been reported.[5] Our results suggest that the electron acceptor property of the CO group contributes to this reduction. The interaction between $3b_2$ of 5 and a CO fragment will transfer electron density from the $3b_2$ orbital at the bicyclobutyl site into the π^* orbital of the carbonyl group and thus reduce the antibonding contribution of the $3b_2$ of 5 to the 1,5 σ bond.

From the orbital sequence predicted for 1 we expect an electrophilic attack at the bicyclobutane moiety. This implies a different behavior for 1 compared with benzvalene.[3,8]

Calculations

Since the geometry of 1, 3, and 4 is not known, we minimized the heat of formation of 1–4 with respect to their geometrical parameters using the MINDO/3 me-

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thod.[7] The most relevant data found for 1–4 are shown in Table II. The calculated bond lengths for 2 compare reasonably well with those reported from X-ray investigations.[5]

Experimental Section

The PE spectra of 1 and 2 were recorded on a PS18 photoelectron spectrometer (Perkin-Elmer Ltd., Beaconsfield) at room temperature. Calibration was achieved with argon and xenon. A resolution of about 20 meV on the $^2P_{3/2}$ Ar line was obtained.

The sample of 1 contained a trace of benzene (see Figure 1). Compounds 1 and 2 were prepared by the methods described previously in the literature.[9,10]

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Registry No. 1, 63001-13-8; 2, 3350-02-5; 3, 87803-52-9; 4, 31519-30-9.

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Notes

Easy Synthesis of a Structural Isomer of Citronellal

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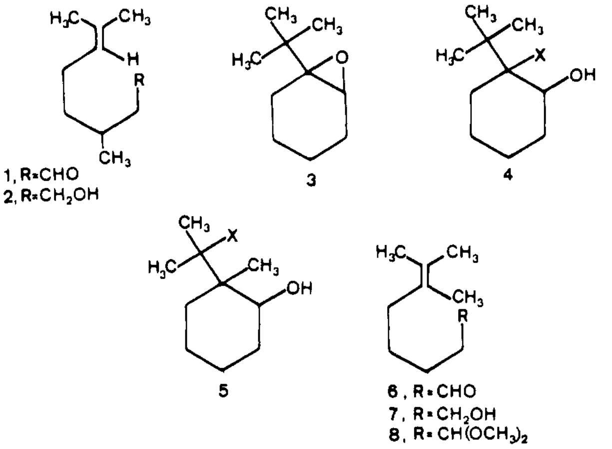
The well-known monoterpene citronellal (1, Chart I) is one of the unsaturated aldehydes naturally occurring in essential oils such as Citronella and Lemongrass oils.[1] Few structural isomers either of 1 or of its corresponding alcohol citronellol (2) have been found in nature or have been synthesized.

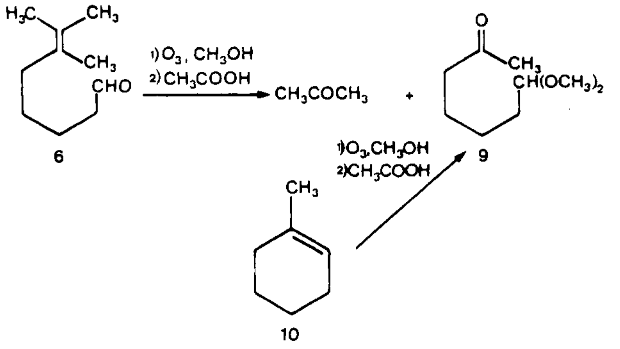
In the course of our studies on the mechanism and the stereochemistry of the reactions of substituted oxiranes under acidic conditions,[2] we examined 1-*tert*-butylcyclohexene oxide (3), structurally analogous to other oxiranes previously examined.[2] The large steric hindrance of the *tert*-butyl and the possibility of 1,2-shifts in the intermediate carbocation formed in the oxirane ring-opening process led us to anticipate that the chemical behavior of 3 could be different from that of other simple alkyl-substituted oxiranes.[2]

The reactions of 3 under acidic conditions afforded complex mixtures[3] consisting of the primary 1,2-addition products (4), the secondary 1,3-addition products (5), which can be assumed to be originated by rearrangement of the original skeleton of 3 by migration of a methyl, and other rearrangement products.[4] Somewhat surprisingly, among these last compounds, the aldehyde 6, which lacks both the *tert*-butyl group and the cyclohexane skeleton, was isolated. The aldehyde 6 is a structural isomer of citronellal (1) and differs from 1 only in the position of one methyl group. The amount of 6 formed in the reactions of 3 changes markedly with the reaction conditions. In the trichloroacetolyses of 3 in nonprotic solvents the amounts of 6 are noticeable: when the reaction is carried out in CH_2Cl_2, the aldehyde 6 is the main product (42% yield, GC). When the acid-catalyzed ring opening of 3 is carried out in methanol or in methanol containing solvents, the dimethyl acetal of 6 (8) is obtained. The structure of the aldehdye 6 has been clarified by its ^{1}H NMR and mass spectrum and unequivocally confirmed through chemical transformations. The aldehyde 6 can be easily transformed into its dimethyl acetal 8 by treatment with anhydrous methanol in the presence of a catalytic amount of sulfuric

Chart I



Scheme I



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(3) The complete details and the mechanism and the stereochemistry of the reactions of epoxide 3 will be published in a forthcoming publication.

(4) The ring-opening reactions of 3 are largely regioselective; the large majority of the reaction products arises from the ring opening between the oxirane oxygen and the tertiary carbon.[3]

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