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SPECTRAL PROPERTIES OF *exo*- AND *endo*-TRICYCLO[3.2.1.0^{2,4}]OCTAN-8-ONES

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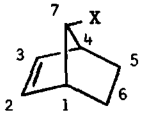
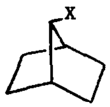
The interaction of formally nonconjugated p-orbital systems has been observed in ultraviolet spectra (*e.g.*, changes in n → π* and π → π* transition energies and intensities for C=C-C-C=O structures (2)) as well as in increased rates of carbonium ion reactions (*e.g.*, solvolysis of homoallylic structures C=C-C-C-X (3)). The most outstanding example of the latter effect is in solvolysis of *anti*-7-norbornenyl (I) and 7-norbornyl (II) derivatives where orbital overlap at the transition state results in a relative rate factor, k_I / k_{II} , of 10^{11} (4). As the interaction of especially oriented p-like cyclopropane orbitals (5) can also give rise to extremely great relative reactivities (k_{III} / k_{IV} = *ca.* 10^{14})(6), it is of interest to determine if the spectra of the corresponding ketones also give evidence of cyclopropyl-carbonyl electronic interactions.



I



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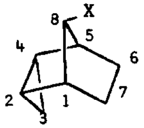

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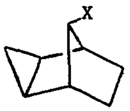
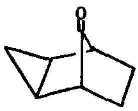
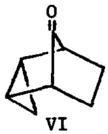


IV

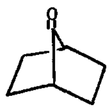
Interestingly, the ultraviolet spectra of the *exo* and *endo* cyclopropyl ketones, V and VI, are almost identical, respectively, to the spectra of ketones VII and VIII. The observed hypsochromic shift for the n → π* transition of olefinic compound VIII relative to the



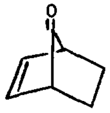
V



VI



VII



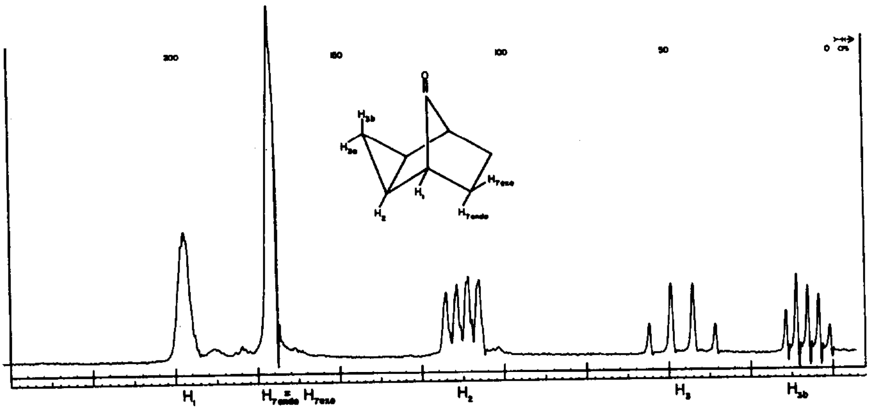
VIII

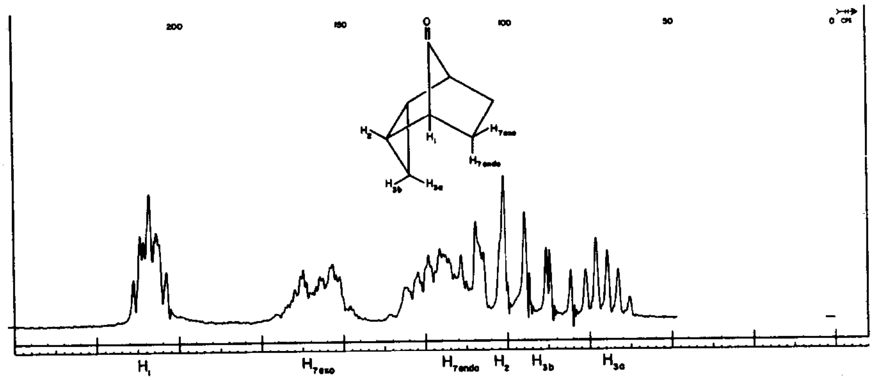
λ_{max}(mμ)(7)	293 (ε22)	276 (ε44)	290 (ε14)	274 (ε36)
λ (mμ)	215 (ε63)	215 (ε495)	215 (ε33)	215 (ε500)

saturated norbornone (VII), although opposite to that found in general for nonplanar β,γ-unsaturated ketones (3,8), has been shown to be consistent with a LCAO-MO treatment involving p_π-p_π and p_σ-p_σ interactions between atoms C2-C7 and C3-C7 in the specific geometry of the norbornene structure (9). The close spectral resemblance of the endo cyclopropyl and norbornenyl ketones (VI and VIII) suggests a similar interaction in which relatively less p-orbital character at atoms 2 and 4 in VI is compensated by being more favorably directed towards the C8 carbonyl orbital (10). The cyclopropyl orbitals of the exo ketone V, are, of course, not directed towards the carbonyl group at all and its spectrum is like that of the saturated 7-norbornone VII (12).

The spectral resemblances of V and VII and of VI and VIII add a new set of analogous properties to the recently reported (6) kinetic properties of the corresponding derivatives IV and II and of III and I. The origin of the analogous properties is apparently the same; in compounds I and III an accelerative electron donation by a double bond or a endo cyclopropyl ring to the incipient carbonium ion during solvolysis, and in compounds VIII and VI an interaction by the double bond or endo cyclopropyl ring p-orbitals in modifying the relative energy of electronic states (13). However, the existence of such analogous properties gives no distinct information concerning the symmetry of the electron donation in the transition states or intermediates for solvolysis of I and III (e.g., in compound III from one of atoms C2 or C4 or equally from both (6,15)).

The n. m. r. spectra of the two cyclopropyl ketones (V and VI) also show interesting dissimilarities. In $DCCl_3$, the 100 Mcps spectrum of exo compound V is remarkably simple (see Figure). The anisotropic magnetic effects of the cyclopropyl group apparently shift the normally higher field (16) endo norbornyl protons (H_{7endo}) downfield to where they have the same chemical shift as the exo protons (H_{7exo}). This fortuitous effect, combined with the unfavorable dihedral angle for H_1-H_2 spin coupling (16), results in a relatively narrow, unsplit absorption for the bridgehead (H_1) protons. The paramagnetic effect of the 8-keto group (17) shifts both the H_{3a} and H_{3b} protons to high field, but the closer H_{3b} proton is shifted to a greater extent. They are both coupled to the two H_2 protons and each presents a pair of overlapped triplets, J_{3a-2}= 6.7, J_{3b-2}= 3.4 and J_{3a-3b}= 6.7 cps (18). In contrast, the endo ketone in $DCCl_3$ shows a very complex spectrum even at 100 Mcps (see Figure). Here a difference in the chemical shifts of exo and endo C7 protons appears (due in part to positioning of the endo protons in the shielded volume above the plane of the cyclopropyl ring (19)), and there is a





decreased difference in the H_{3a} and H_{3b} protons (now both away from the field of the carbonyl group). These relative changes in orientation of anisotropic groups result in a more "compressed" spectrum for endo ketone. In addition, a smaller dihedral angle between H_1 and H_2, and the lack of the accidental equivalence of chemical shifts which gives rise to the exceptionally simple spectrum of exo ketone, results in the many spin-spin splittings apparent with the endo ketone.

In benzene, when intervention by the anisotropic solvent molecules no longer allows the same chemical shift for $H_{7\underline{exo}}$ and $H_{7\underline{endo}}$, the n. m. r. spectrum of the exo ketone developes most of the complexities of its endo isomer. The $H_{7\underline{exo}}$ and $H_{7\underline{endo}}$ protons now appear as a complex multiplet at 1.5 to 1.25 ppm (downfield from TMS) while the difference in positions of the geminal protons 3a and 3b is practically eliminated and they make their entangled appearance at ca. 0.35 to 0.1 ppm.

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(7) Spectra taken in 95% ethanol. The values given for VIII are taken from the reported spectrum (ref.9) and from a private communication from Dr. B. Franzus. The spectra of VII and VIII agree with those reported by R. K. Bly and R. S. Bly, *J. Org. Chem*., **28**, 3165 (1963) and P.G. Gassman and P. G. Pape, *ibid*., **29**, 160 (1964).

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(10) The requirement for maximum delocalization in α,β-cyclopropanoketones is that the plane of the π bond of the carbonyl function and the plane of the cyclopropyl group have a "parallel" relationship (11). In the β,γ-cyclopropanoketone VI these planes have an "orthogonal" relationship. However, at the greater distance between p-orbitals in VI, sigma-type interaction is more important than pi-type interaction and the orthogonal arrangement points *both* of the C2-C4 cyclopropyl orbitals towards the C8 carbonyl orbital.

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(13) Some ground state interaction of the carbonyl and cyclopropyl groups in compounds V and VI is shown by a relative change in their infrared carbonyl stretching frequencies. The strongest peak in *exo* ketone V is at 15 cm^{-1} less wavenumbers than with the *endo* ketone VI (14). However, typically for bridged carbonyl groups, each compound has several carbonyl peaks or shoulders (ν_{max} in CCl_4: V 1859w, 1813w, 1775s, 1743m, 1724w; VI 1858w, 1818m, 1760s, 1725w) and the origin of the relative change can not be distinctly ascribed to resonance effects (possible in *endo* ketone), to stereoelectronic effects (possible in *exo* ketone)or to coupled vibrations (possible in either ketone).

(14) Resonance in directly conjugated cyclopropyl ketones results in *ca*. 20 cm^{-1} lower carbonyl frequency, see R. H. Eastman and S. K. Freeman, *J. Am. Chem. Soc*., **77**, 6642 (1955).

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(18) Spin decoupling experiments show that in addition to coupling to the H_3 protons, the H_2 protons in *exo* ketone are weakly coupled to the two H_1 bridgehead protons, $\frac{1}{2}(J_{1-2} + J_{4-2}) =$ *ca* 0.8 cps, resulting in broadening for H_1 and triplets for each of the four lines of H_2.

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