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Homoconjugation in Bicyclo[3.2.1]octa-3,6-dien-2-yl and 6,9-Dihydro-5,9-methano-5*H*-benzocyclohepten-6-yl Radicals as Studied by Electron Spin Resonance[1)]

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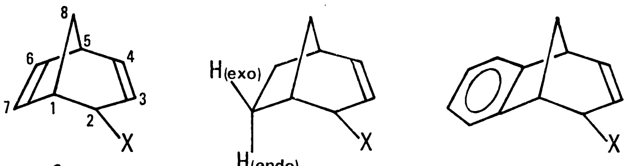
Synopsis. The radicals in the title and the bicyclo[3.2.1]oct-3-en-2-yl radical are examined with ESR. The extent of the odd electron delocalization due to π-π homoconjugation in the bicyclo[3.2.1]octa-3,6-dien-2-yl radical is estimated to be in the order of a few per cent.

Brown and Occolowitz[2)] found an enhanced reactivity of bicyclo[3.2.1]octa-2,6-diene (**1h**) in a base-catalyzed allylic-proton exchange in comparison with that of bicyclo[3.2.1]oct-2-ene (**2h**). This was attributed to a strong π-π homoconjugation in the intermediate anion, **1a**. A similar but somewhat damped homodelocalization was reported for **3a** by Rosenthal and Winstein.[3)]



1 **2** **3**

h: X = H, **a**: X = ⊖, **r**: X = •

Scheme 1.

Experimental evidence for the homodelocalization in **1a** was given by its ^{1}H NMR spectrum.[4)] However, Trimitsis and Tuncay[5)] reported that long-range π interactions can not be safely concluded by examining only the ^{1}H NMR of the anions.

We have now examined the homoconjugation involved in **1r** and **3r** by comparing their ESR spectra with that of **2r**. Toward the end of our study, a paper by Sustmann and Gellert[6)] appeared reporting a study similar to ours. Our analysis of the spectrum of **2r** is, however, somewhat different from that of Sustmann and Gellert, although the difference is not very important for the analysis of the homoconjugation.

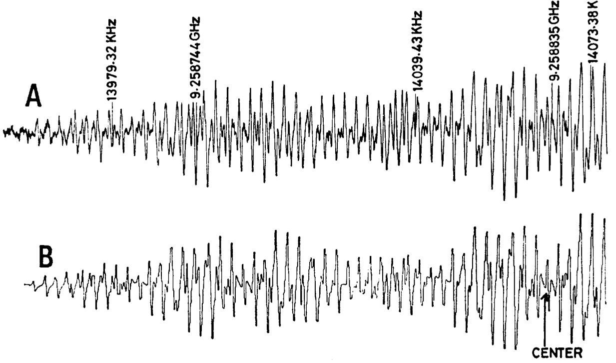


Fig. 1. Low-field half of observed (A) and simulated (B) spectra of **2r**. The numbers at markers in kHz and GHz units are ^{1}H NMR radio and ESR microwave frequencies, respectively.

An ESR spectrum of **2r** (Fig. 1) was observed during the photolysis of a cyclopropane solution of a mixture of **2h** and di-*t*-butyl peroxide at −120 °C. The spectrum was analyzed as 14.32 (2H), 4.93 (2H), 3.19 (1H), 1.80 (2H), 1.11 (1H), 1.02 (1H), and 0.54 G (2H). The *g* factor was 2.00256. A comparison of these hyperfine splitting constants (hfsc) with those of allylic cycloalkenyl radicals[7)] leads to the assignments of $a(H_2)=14.32$ and $a(H_3)=3.19$ G. The remaining two sets of doublets (1.11 and 1.02 G) are due to two protons on C_8. The hfsc of the triplet of 4.93 G is about a half of that of the exo-6 proton of the 2-norbornyl radical,[8)] suggesting an assignment to H_{6exo}. The triplet of 1.80 G is attributed to the bridgehead protons because triplet splittings of *ca.* 1.8 G were observed in the spectra of **1r**—**3r** (*vide infra*). The remaining triplet of 0.54 G is due to endo-6 and -7 protons. The **1r** and **3r** radicals were generated by the removal of a hydrogen atom by the *t*-butoxy radical from **1h** and **3h** respectively. The resolved hfsc's of **1r** and **3r** and their assignments are listed in Table 1, together with those of **2r**.

TABLE 1. OBSERVED hfsc's OF **1r**, **2r**, AND **3r**

Radical	*g*	*a*(H)[a)]				
		H_2	H_3	H_1	H_6	H_8
2r	2.00256	14.32	3.19	1.80	4.93[b)] 0.54[c)]	1.11 1.02
3r	2.00272	14.23	3.19	1.78		1.21[d)]
1r	2.00276	14.07	3.25	1.87	1.35	1.35[d)]

a) In G units. b) *exo* protons. c) *endo* protons.
d) Two nonequivalent protons have, accidentally, the same hfsc.

The hfsc of H_6 of **1r** has a magnitude between those of H_{6endo} and H_{6exo} of **2r**, in which the π-π homoconjugation is not involved. Thus, the extent of the homoconjugation can not be deduced directly from the hfsc of H_6 of **1r**. These is a shift in $a(H_2)$ in the order of **2r**>**3r**>**1r**. There exists a possibility that this is due to strain exerted on the allylic moiety, because this is the decreasing order of the bond length between C_6 and C_7. The hfsc's of the protons on the terminal carbon atoms of allylic moieties in the cyclohexenyl and in the more strained cyclopentenyl radicals are quite similar (14.35 and 14.30 G respectively),[7)] implying that the observed shift of $a(H_2)$ of **1r**—**3r** is not likely to originate from the change in the geometry of the allylic moiety in these radicals.

Another possible origin of the shift of $a(H_2)$ is the delocalization of the odd electron from the allylic π system onto the etheno or benzo bridge. To examine this possibility, logarithms of the relative reactivities of **1h**—**3h** in the base-catalyzed allylic-proton exchange[2,3] were plotted against the values of the $a(H_2)$ of the corresponding radicals in Fig. 2. The fair correlation in Fig. 2 impies that the π-π homoconjugation in **1r** and **3r** is dominant, but not strong enough to exceed sufficiently other factors in shifting $a(H_2)$ and/or that the homoconjugation in anions is not linearly related to that in radicals.

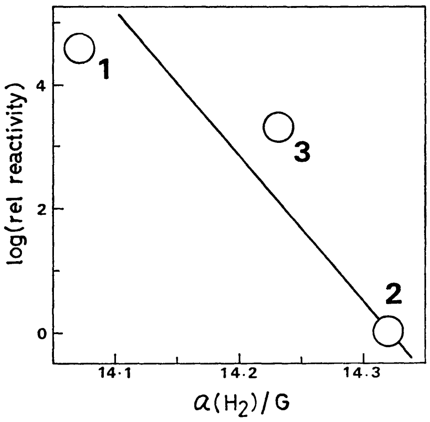


Fig. 2. Relation between kinetic acidity of olefin and hfsc of H_2 of the corresponding radical.

The odd electron density in the allylic π system can reasonably be expected to be proportional to $a(H_2)$; the odd electron density in the allylic π system of **1r** is estimated to be around 2% less than that of **3r**. This 2% decrease would more or less reflect the extent of the π-π homoconjugation in **1r**, as is suggested by the fair correlation between $a(H_2)$ and the kinetic acidity. Thus, we conclude that the extent of the odd electron delocalization from the allylic π system to the π system of the etheno bridge in **1r** is of the order of a few per cent, corresponding to the resonance integral (in Hückel approximation) between π atomic orbitals (AO) on C_2 and C_7 (β_{27}) of a magnitude of 5—20% of the integral between π AO's involved in a carbon-carbon double bond (β).

Experimental

Three hydrocarbons, **1h**,[9] **2h**,[9] and **3h**,[10] were prepared according to known procedures. The equipment and procedures for the photolysis-ESR experiments have been described earlier.[11]

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