

Carbon Orbital Hybridizations and Acidity of the Bicyclobutane System

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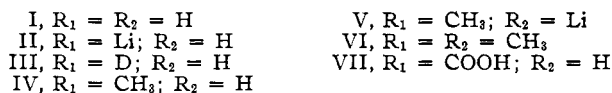
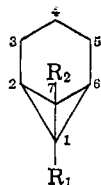
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The remarkably high degree of s-character of the C_1 -H bond led us to expect unusual acidity of the hydrocarbon. This prediction was verified when it was observed that I reacted with *n*-butyllithium in ether to form quantitatively the bicyclobutyl lithium II,⁸ from which I could be regenerated on hydrolysis, and which was converted to III on treatment with deuterium oxide. The n.m.r. spectrum of III establishes the position of the deuterium atom, since the triplet at 8.55 τ in the spectrum of I, attributed to the protons at positions 1 and 7, is replaced in the spectrum of III by an unresolved multiplet of one half the intensity.⁹ Reaction of II with methyl iodide gave IV (b.p. 66° (100 mm.), n_D^{20} 1.4580; n.m.r. (CCl₄) 7.86 (m), 8.48 (s), 8.75 (m), 9.00 (t) τ , relative areas 2:3:6:1), while carbonation yielded VII (m.p. 84.5–86.0°; n.m.r. (CCl₄) –1.90 (s), 6.89 (m), 7.75 (t), 8.55 (m) τ , relative areas 1:2:1:60; ultraviolet (pentene) end abs. 220 $m\mu$, ϵ 7,700; pK_a 4.6). The carbon-13 hydrogen coupling constants at positions 2 and 7 in IV are identical within experimental error with those measured for I. Again, the high degree of s-character of the C_7 -H bond in IV is reflected in the reaction with *n*-butyllithium yielding V. Treatment of V with methyl iodide resulted in the formation of VI (b.p. 72° (20 mm.); n_D^{20} 1.4529; n.m.r. 8.20 (m), 8.73, (s), 8.76 (m) τ , relative areas of the 8.20 signal to the sum of the 8.73 and 8.76 peaks 1:6.¹⁰

Further evidence for the acidity of the bicyclobutane system was obtained from deuterium-hydrogen exchange studies on III carried out in *t*-butyl alcohol with potassium *t*-butoxide as catalyst. Conversion of III to I follows first-order kinetics (k_1 at 99.5° and 0.61 mole/l. potassium *t*-butoxide = 2×10^{-7} sec.⁻¹).

The results reported here are in qualitative agreement with the generally accepted theory of bonding in small ring compounds¹¹ which predicts unusually high degree of s-character for the exocyclic carbon orbitals. Comparison of the data with those obtained for 1,3,3-trimethylcyclopropene (¹³C₁-H 220 c.p.s., corresponding to 44% s-character³; deuterium-hydrogen exchange approximately 10⁴ times faster than III) indicates a certain qualitative analogy between the two ring systems. However, it remains to be established whether the considerably larger exchange rate of the cyclopropene is caused mainly by the somewhat higher

s-character of the =C-H bond, or whether the induc-

tive effect of the double bond is a strongly contributing factor.

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The Temperature-Independent Factor of the Kinetic Isotope Effect¹

Sir:

In eq. 1 for the kinetic isotope effect in terms of vibration frequencies of reactants and activated com-

$$\frac{k}{k'} = \frac{\nu_L^*}{\nu_L'^*} \prod_i \frac{\nu_i^*}{\nu_i'^*} e^{-\Delta u_i^*/2} \frac{(1 - e^{-u_i'^*})}{(1 - e^{-u_i^*})} \prod_i \frac{\nu_i'}{\nu_i} e^{\Delta u_i/2} \frac{(1 - e^{-u_i})}{(1 - e^{-u_i'})}$$

plex, the factor $\nu_L^*/\nu_L'^*$ has been widely designated^{2,3} as "the temperature-independent factor." Bigeleisen and Wolfsberg² derived expression 2 for this factor for a linear triatomic activated complex with masses m_1 ,

$$\frac{\nu_L^*}{\nu_L'^*} = \left[\frac{(\mu_{23} + p\mu_{12} + 2p^{1/2}\mu_2)}{(\mu_{23}' + p\mu_{12}' + 2p^{1/2}\mu_2')} \right]^{1/2} \quad (2)$$

m_2 and m_3 and internuclear distances r_1 and r_2 , where $\mu_{12} = m_1^{-1} + m_2^{-1}$, $\mu_{23} = m_2^{-1} + m_3^{-1}$, $\mu_2 = m_2^{-1}$, and $p^{1/2}$, which equals β/α , "determines the relative amount of bond formation to bond rupture"² in the reaction coordinate $x_L = \alpha r_2 - \beta r_1$. Yankwich and Ikeda⁴ extended the calculation to other transition-state geometries and to $n = 4$.

The actual temperature-independent factor obtained by extrapolation is, however, not usually $\nu_L^*/\nu_L'^*$ at all, but depends on the experimental conditions and the extrapolation method. If all real vibration frequencies of both reactants and transition state are greater than about $6kT/h$, eq. 1 becomes

$$k/k' = \tau_* \tau_i^{-1} e^{-\left[\sum_i^{3n^*-7} \Delta u_i^*/2 - \sum_i^{3n-6} \Delta u_i/2 \right]} \quad (3)$$

$$\tau \equiv \prod_i^{3n-6} \nu_i/\nu_i' \quad (4)$$

where the symbols * and r refer to transition state and reactants, respectively. Under these conditions (high frequencies or low temperature), $\ln(k/k')$ vs. $1/T$ is linear with infinite-temperature intercept $\ln \tau_* \tau_i^{-1}$. For the linear triatomic activated complex the contribution to τ_* from the two linear vibrations (one of which is $\nu_L^*/\nu_L'^*$) can be calculated, most easily by the FG-matrix method of Wilson, Decius and Cross,⁵ to be

$$\nu_1 \nu_2 / \nu_1' \nu_2' = [(\mu_{12} \mu_{23} - \mu_2^2) / (\mu_{12}' \mu_{23}' - \mu_2'^2)]^{1/2} \quad (5)$$

Note that this is entirely independent of any structural features of the transition state other than the masses and their mutual ordering. Evidently the variations with transition-state structure which are predicted for the imaginary-frequency ratio by eq. 2 are precisely cancelled by converse variations in the other linear-fre-

(8) At 25° and concentrations of 1 mole/l. of each reactant, the half-reaction point is reached after approximately 3 hr.

(9) The n.m.r. spectrum of I reported by Moore¹ for the neat compound consists of three signals, 7.58 (m) for protons at carbon 2 and 6, 8.33 (t) for protons at 1 and 7 and 8.55 (m) τ for the methylene protons. These values change in carbon tetrachloride to 7.72, 8.55 and 8.71 τ . The assignments of the resonances made by Moore were further supported by spin decoupling experiments carried out in our Laboratory. It was shown that the protons giving the signal at 7.72 τ are coupled with both the methylene protons and the protons whose signal appears at 8.55 τ . The latter are only coupled with the 7.72 resonance.

(10) Compounds I, III, IV and VI were purified by vapor phase chromatography. Satisfactory analyses were obtained for all new compounds.

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(1) Supported in part by the Atomic Energy Commission under Contract No. AT(30-1)-905.

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