Acidity of Hydrocarbons. XXXI. Kinetic Acidities of Small-Ring Cycloalkanes and Correlation with J(^{13}C–H)[1]

Sir:

Although the stability of carbanions with localized charge is known to depend qualitatively on the amount of s character in the lone pair,[2] few quantitative correlations are available.[3] We report here the kinetic acidities of the cycloalkanes from cyclopropane to cyclooctane as measured by cesium cyclohexylamide (CsCHA) catalyzed tritium incorporation from N-tritiated cyclohexylamine. Cyclopropane and cyclobutane were exchanged with benzene as a standard, and kinetic aliquots were measured by radio-gas chromatography.[4] The other cycloalkanes were exchanged as mixtures with cyclohexane, as described previously for cyclopentane and cycloheptane.[1b] The reactivities cover a range of 10^5 in rate and are summarized in Table I.

Table I. Kinetic Acidities of Hydrocarbons toward Cesium Cyclohexylamide at 50°

Hydrocarbon	Relative rate	J(^{13}C–H)
Cyclopropane	$(7.0 \pm 0.9) \times 10^4$	161[a]
Cyclobutane	28 ± 10	134[b]
Cyclopentane	5.72 ± 0.27	128[a,b]
Cyclohexane	1.00	123,[a] 124[b]
Cycloheptane	0.76 ± 0.09	123[b]
Cyclooctane	0.64 ± 0.06	122[b]

[a] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959). [b] C. S. Foote, *Tetrahedron Letters*, 579 (1963).

Closs and Larrabee[3] found previously a quantitative correlation of kinetic acidities of some bicyclobutane and cyclopropene derivatives with the appropriate J(^{13}C–H). For the cycloalkanes, such coupling constants, which appear to be valid measures of s character in hydrocarbons, are included in Table I; Figure 1 contains a plot of log relative rate against these coupling constants. The linear correlation obtained indicates that the dominant factor in cycloalkane acidity is the amount of s character in the exocyclic C–H bond.

A simple extrapolation gives a reactivity of 7×10^5 for C_{sp^2}–H relative to cyclohexane, or 0.008 relative to benzene. Previously, we applied a simple field-effect function to the kinetic acidity of arene hydrogens toward lithium cyclohexylamide (LiCHA).[5] An extrapolation of this correlation to zero field effect gives a reactivity of 0.025 relative to benzene for an isolated C_{sp^2}–H. Thus, two independent approaches give about the same value for the kinetic acidity of a trigonal C–H bond. This agreement also indicates that both of these kinetic acidity measures are scaled similarly, *i.e.*, cycloalkanes with CsCHA and arenes with LiCHA have similar Brønsted coefficients.

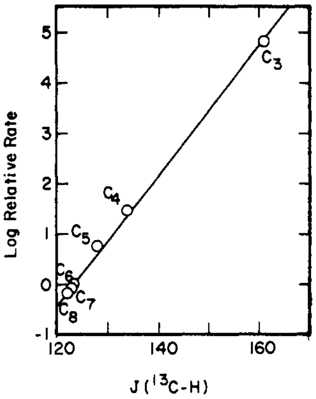

Figure 1. Correlation of tritium exchange rates with CsCHA of cycloalkanes compared to J(^{13}C–H). The least-squares line is log relative rate = $(0.129 \pm 0.003)J(^{13}\mathrm{C{-}H}) - 15.90 \pm 0.38$; standard deviation, 0.095; correlation coefficient, 0.999.

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(2) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 48.

(3) G. L. Closs and R. B. Larrabee, *Tetrahedron Letters*, 287 (1965).

(4) A. Streitwieser, Jr., and H. F. Koch, *J. Am. Chem. Soc.*, **86**, 404 (1964).

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(6) National Science Foundation Predoctoral Fellows: (a) 1961–1964; (b) 1964–1967.

Andrew Streitwieser, Jr., Richard A. Caldwell,[6a] William R. Young[6b]
Department of Chemistry, University of California
Berkeley, California 94720

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Acidity of Hydrocarbons. XXXII. Kinetic Acidities of Medium-Sized Cycloalkanes. Pyramidal Alkyl Anions[1]

Sir:

We report here the kinetic acidities of medium-ring cycloalkanes from C_9 to C_{14} by the cesium cyclohexylamide (CsCHA) catalyzed tritiodeprotonation method previously developed with cyclohexane[2] and other cycloalkanes. In this series internal strains from hydrogen oppositions vary substantially, but hybridization differences (as measured by J(^{13}C–H)) are small (Table I).

The hydrocarbons were obtained commercially or synthesized in standard ways. Alkene impurities were removed by successive treatments with potassium permanganate and sulfuric acid and the final products were obtained by glpc or by sublimation. A mixture of hydrocarbons was treated kinetically with CsCHA in cyclohexylamine-N-*t* as described previously[1b,2] to give directly the relative rates summarized in Table I.

Reactions involving carbonium ions and radicals generally show enhanced rates for the medium-ring cycloalkyls with peaks close to cyclodecane. Examples are the acetolyses of cycloalkyl tosylates[3,4] and the

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(1) (a) This research was supported in part by Grant GM-12855 of the National Institutes of Health, U. S. Public Health Service. (b) Paper XXXI: A. Streitwieser, Jr., R. A. Caldwell, and W. R. Young, *J. Am. Chem. Soc.*, **91**, 529 (1969).

(2) A. Streitwieser, Jr., W. R. Young, and R. A. Caldwell, *ibid.*, **91** 527 (1969).

(3) H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

(4) R. Heck and V. Prelog, *Helv. Chim. Acta*, **38**, 1541 (1955).

Table I

Cycloalkane, *n*	Rel rate, CsCHA, 100°	Strain per methylene, kcal/mol[d]	$J(^{13}C-H)$, cps
6	1.00	0	124,[e] 124 ± 3[f]
7	0.76 ± 0.09[a,b]	0.9	123[e]
8	0.64 ± 0.06[a,b]	1.2	122[e]
9	1.01 ± 0.07[a]	1.4	124 ± 3[f]
10	0.73 ± 0.05	1.2	118,[e] 121 ± 3[f]
11	0.60 ± 0.03	1.0	122 ± 3[f]
12	0.48 ± 0.05[c]	0.3	123,[e] 121 ± 3[f]
13		0.4	
14	0.345 ± 0.026	0	126 ± 4[f]

[a] At 50°. [b] From ref 1b. [c] 0.48 ± 0.02 at 50°. [d] J. W. Knowlton and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **43**, 113 (1949); S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.*, **71**, 261 (1952); J. Coops, H. van Kamp, W. A. Lambregts, B. J. Visser, and H. Dekker, *ibid.*, **79**, 1226 (1960). [e] C. S. Foote, *Tetrahedron Letters*, 579 (1963). [f] F. J. Weigert and W. R. Young, unpublished results.

thermolyses of bis(azocycloalkylnitriles).[5] In these cases the transition state resembles a planar carbonium ion or radical in which hydrogen opposition strains are reduced. By contrast, the kinetic acidities show comparatively little change along this series. The larger cycloalkanes are somewhat less reactive than cyclohexane toward CsCHA, but the $J(^{13}C-H)$ values tend to be somewhat lower, indicative of less s character in the C–H bonds.[1b] The contrast between the carbanion and carbonium ion reactions is shown in Figure 1 in which the relative rate pattern for the CsCHA exchange reactions is compared to the cycloalkyl tosylate acetolysis rates. We conclude that the transition states for the CsCHA exchange reactions have conformations little different from the ground states and that, therefore, the *carbanion intermediates are pyramidal.* Note that the relatively high primary isotope effect reported previously for cyclohexane[2] implies that the transition state has substantially the structural character of the carbanion intermediate.

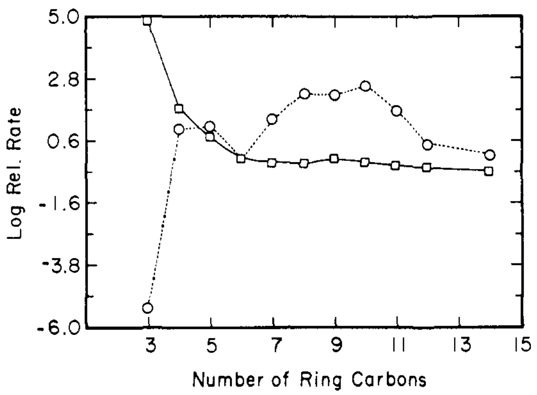

Figure 1. Comparison of relative rate pattern with ring size for acetolysis of cycloalkyl tosylates (broken line, circles) with CsCHA-catalyzed tritiodeprotonation (unbroken line, squares).

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(5) C. G. Overberger, H. Biletch, A. B. Firestone, V. Lilker, and J. Herbert, *J. Am. Chem. Soc.*, **75**, 2078 (1953).

(6) National Science Foundation Predoctoral Fellow, 1964–1967.

Andrew Streitwieser, Jr., William R. Young[6]
Department of Chemistry, University of California
Berkeley, California 94720

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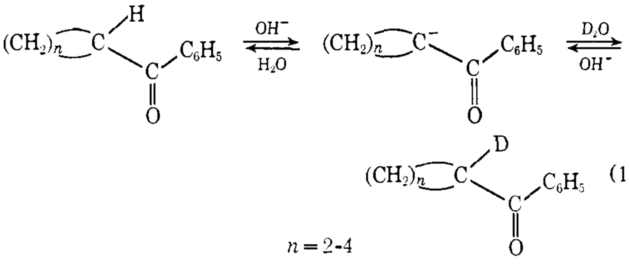
Investigation of Base-Catalyzed Enolization of Cyclopropyl Ketones

Sir:

It has been reported[1] that the first-order rate constants for base-catalyzed isotopic exchange of methine hydrogen of homologous cycloalkyl phenyl ketones in deuterium oxide–triethylamine–dimethylformamide decrease as the ring size increases: three > four > five > six, approaching the open-chain analog isobutyrophenone as an approximate limit (eq 1). The results obtained from cyclopropyl phenyl ketone are rationalizable on the basis of the s character of the carbon orbital involved in bonding with the potential enolizable hydrogen[2a] (eq 1), the report that the kinetic acidity of cyclopropane is larger than that of its higher and open-chain analogs,[2b] and the observations that base-catalyzed deuterium exchange occurs considerably faster in 2-2-diphenylcyclopropyl cyanide than in 2-methyl-3,3-diphenylpropionitrile[2c] and in cyclopropyl phenyl sulfone than in isopropyl phenyl sulfone.[2d] The behavior of cyclopropyl phenyl ketone is inconsistent, however, with experiments that reveal that nitrocyclopropanes resist neutralization and base-catalyzed deuterium exchange and are much weaker protonic acids than are their homologous or acyclic analogs,[3] and salts of cyclopropanecarboxylic acid do not undergo isotopic exchange in deuterium oxide at temperatures in which deuterium incorporation into its higher homologs and to salts of isobutyric acid is extensive.[4]



(1)

The above results have led to investigation of possible deuterium exchange for methine hydrogen in cyclopropyl phenyl ketone, isobutyrophenone, dicyclopropyl ketone, and diisopropyl ketone as catalyzed by deuterioxide ion at 60° in deuterium oxide and purified dimethylformamide. Samples of the kinetic mixtures, as

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(2) (a) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, 40, 1 (1949); (b) E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, p 28, and references therein; (c) H. M. Walborsky, A. A. Youssef, and J. M. Motes, *J. Amer. Chem. Soc.*, **84**, 2465 (1962); (d) R. Breslow, J. Brown, and J. J. Gajewski, *ibid.*, **89**, 4383 (1967).

(3) H. B. Hass and H. Shechter, *ibid.*, **75**, 1382 (1953); (b) H. Stone, Ph.D. Dissertation, The Ohio State University, 1950; (c) P. W. K. Flanagan, Ph.D. Dissertation, The Ohio State University, 1957; (d) H. W. Amburn, Ph.D. Dissertation, The Ohio State University, 1968.

(4) (a) A. P. Bottini and A. J. Davidson, *J. Org. Chem.*, **30**, 3302 (1965); (b) J. G. Atkinson, J. J. Csakvary, G. T. Herbert, and R. S. Stuart, *J. Amer. Chem. Soc.*, **90**, 498 (1968).