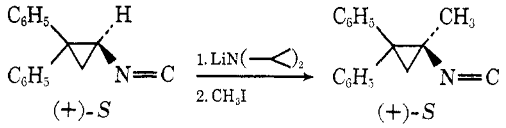
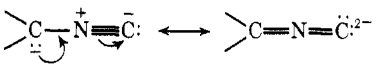
Table I. Effect of Temperature on Racemization of **4**



Temp, °C	Yield, %	Optical purity, %[a]
−72 ± 2	96	98
−52 ± 1	75	93
−5 ± 1	80	0.3

[a] Optically pure 2,2-diphenylcyclopropyl isocyanide has $[\alpha]^{25}{}_{\mathrm{Hg}}$ 353 ± 2° (*c* 0.43, $CHCl_3$); optically pure 1-methyl-2,2-diphenylcyclopropyl isocyanide has $[\alpha]^{25}{}_{\mathrm{Hg}}$ 166 ± 1° (*c* 1.0, $CHCl_3$).



would not be expected to contribute much to the overall stability of the anion. The loss of configuration at −5° indicates that the isocyano group is better than the methyl group in lowering the energy barrier to inversion of configuration in this system.[3] Further studies on the configurational stability of different isocyanocarbanions in protic and aprotic solvents are in progress.

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Kinetic Acidity of Cubane[1]

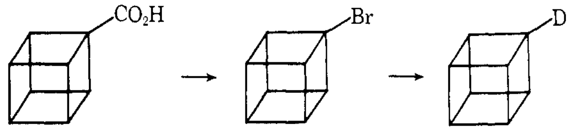
Sir:

Base-catalyzed hydrogen isotope exchange reactions have been widely applied for the study of weak carbon acids.[2] The close relationship between the kinetic acidities of the hydrocarbons based on exchange reactions with nitrogen and oxygen bases and their apparent pK_A values is well documented.[2] Consequently, this method can be used with some confidence to assess the relative strength of new weak carbon acids.

Several factors influence the strength of carbon acids. However, the correlation between the exchange rate and the s character of the exocyclic carbon bonding orbital has proved extremely valuable for the interpretation of the influence of structure on acidity in general[2] and for the analysis of the data for strained ring compounds in particular.[2c,3] A key principle underlying these analyses is that there is a close parallel between the s character in the hydrocarbons and in the derived carbanion. Even though the unshared electron pair would be more stable in an orbital with high s character, rehybridization is usually resisted by substantial forces stemming from serious increases in the energy content of the electrons in the other carbon bonding orbitals. As a result there is little drive for major rehybridization.

Cubane with its novel geometry and large strain energy,[4] 166 kcal mol^{-1}, may provide a different case. In this molecule, rehybridization of the anionic center to an exocyclic orbital with importantly enhanced s character may relieve strain as the endocyclic orbitals acquire greater p character bringing the interorbital angles into better accord with the internuclear angle. We have tested this viewpoint by the study of the kinetic acidity of cubane-*d* in cyclohexylamine.

Cubane carboxylic acid (I) was converted to bromocubane (II) by the Hunsdiecker reaction in 75% yield.[5] The bromide was converted to cubane-*d* (III) in 65% yield with tributyltin deuteride.[6]



I II III

Both kinetic and competitive experiments were carried out to determine the kinetic acidity. Methods similar to those used by Streitwieser and his students were adopted. However, we elected to study the reactions in somewhat greater concentrations of the base to accelerate the exchange reactions. The procedures were tested by the study of labeled benzene, naphthalene, and toluene. In addition, it was established that the cubane was stable under the conditions of these experiments. The results are summarized in Table I.

Table I. Rates and Relative Rates of Exchange of Aromatic Hydrocarbons and Cubane Catalyzed by Lithium Cyclohexyl Amide in Cyclohexylamine at 50°

Compound[a]	Rate constant[b] 10^5k_1, sec^{-1}	Relative rate
Cubane	6.78 ± 0.48 (4)[c]	1.20 (5)[c]
Benzene	5.53 ± 0.05 (3)[c]	1.00
Naphthalene-*1*-*d*		2.3 ± 0.1 (2)[c]
Toluene-*α*-*d*		23 ± 1.0 (3)[c]
Toluene-*4*-*d*		0.29 ± 0.01 (2)[c]

[a] The concentrations were near 0.1–0.3 *M* for the hydrocarbons and 0.15–0.3 *M* for the base. [b] Pseudo-first-order rate constant. [c] Number of observations.

The kinetic acidity of cubane and the other hydrocarbons are compared in Table II.

The results indicate that cubane is as acidic as benzene, about 10^3 more acidic than cyclopropane, about 10^6 more acidic than cyclobutane, and 10^8 more acidic than cyclohexane. The large difference between cyclopropane and cyclohexane has been identified with the

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(1) This research was supported by the National Science Foundation.

(2) (a) A. I. Shatenstein, *Advan. Phys. Org. Chem.*, **1**, 155 (1963); (b) A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, **3**, 41 (1965); (c) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965; (d) H. Fischer and D. Rewicki; *Progr. Org. Chem.*, **7**, 116 (1968); (e) D. J. Cram, *Surv. Progr. Chem.*, **4**, 45 (1968); (f) H. F. Ebel, *Fortschr. Chem. Forsch.*, **12**, 387 (1969); (g) J. R. Jones, *Quart. Rev., Chem. Soc.*, **25**, 363 (1971); (h) J. R. Jones, *Progr. Phys. Org. Chem.*, **9**, 241 (1972); (i) J. R. Jones, *Annu. Rep. Progr. Chem.*, **69A**, 119 (1972); (j) A. Streitwieser, Jr., and P. J. Scannon, *J. Amer. Chem. Soc.*, **95**, 6273 (1973), and earlier papers in this series.

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(4) (a) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. Wertz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971); (b) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *ibid.*, **95**, 8005 (1973).

(5) T. W. Cole, Jr., private communication.

(6) Our experience indicates that the photochemical tin hydride reduction provides a convenient method for the conversion of bridgehead bromides to hydrocarbons: W. P. Neumann and H. Hillgärtner, *Synthesis*, 537 (1971).

Table II. Relative Rates of Exchange for Selected Hydrocarbons in Cyclohexylamine

Compound	Relative rate LiCHA, 50° H/D[a]	CsCHA, 50° H/T[b]	LiCHA, 50° H/D[c]
Benzene-*d*	1.0	1.0	1.0
Naphthalene-*1-d*	6.7		2.3
Toluene-*α-d*	67	110	23
Toluene-*4-d*	0.57	0.46	0.29
Cubane-*d*			1.2
Cyclopropane-*d*		10^{-3}	
Cyclobutane-*d*		10^{-6}	
Cyclohexane-*d*		10^{-8}	

[a] A. Streitwieser, Jr., D. E. van Sickle, and W. C. Langworthy, *J. Amer. Chem. Soc.*, **84**, 244 (1962); A. Streitwieser, Jr., R. G. Lawler, and C. Perrin, *ibid.*, **87**, 5383 (1965); ref 8. [b] A. Streitwieser, Jr., W. R. Young, and R. A. Caldwell, *J. Amer. Chem. Soc.*, **91**, 527 (1969); ref 2c, 3a, 8. [c] This study.

change in s character from 25% s for cyclohexane (J_{CH} = 123 Hz) to 32% s for cyclopropane (J_{CH} = 160 Hz).[7] In a similar manner, the difference between cyclohexane and benzene is related to the altered s character of the carbon bonding orbital with an appropriate correlation for the stabilizing polar influence of the carbon atoms of the aromatic nucleus.[8]

Cubane (J_{CH} = 155 Hz)[9] and cyclopropane have about about 30 and 32% s character, respectively, in their exocyclic carbon bonding orbitals. Consequently, the fact that cubane is about 1000-fold more acidic than cyclopropane is striking. The difference is even more striking in view of the widespread evidence for the idea that alkyl substitution at the anionic site or elsewhere in the molecule decreases the strength of carbon acids. Thus, the 1000-fold difference is, in a sense, a lower limit. We infer that the large enhancement of acid strength originates in the altered hybridization at the anionic carbon atom to an orbital with significantly enhanced s character.

Acknowledgment. We are indebted to Professors P. E. Eaton and A. Eschenmoser for valuable discussions.

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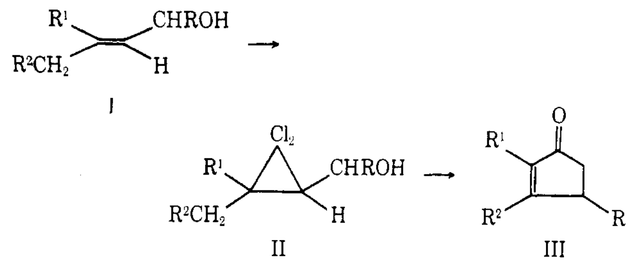
Acid-Catalyzed Reaction of Dichlorocyclopropylcarbinols. Preparation of 2-Cyclopentenones

Sir:

The construction of five-membered rings presents a general attractive problem in organic synthesis in view of the interest in physiologically active natural products which feature this moiety.[1] We wish to report a unique method of synthesizing a cyclopentenone ring (III) based on the one-carbon homologation of an allylic alcohol (I) as shown below.



I

II

III

a, $R^1 = R = Me$; $R^2 = H$
b, $R^1 = Me$; $R^2 = R = H$
c, $R^1 = Me$; $R^2 = n\text{-}C_4H_9$; $R = H$
d, $R^1 = Me$; $R^2 = n\text{-}C_5H_{11}$; $R = H$
e, $R^1 = Me$; $R^2 = CH_2{=}CHCH_2$; $R = H$
f, $R^1,R^2 = \text{-}(CH_2)_{10}\text{-}$; $R = H$

Formation of dichlorocarbene adduct II directly from allylic alcohol I can be accomplished in high yields by the phase transfer method.[2] Although IIa was prepared previously by Seyferth[3] using phenyltrihalomethylmercury, the approach is not practical. Treatment of 4-methyl-3-penten-2-ol and cetyltrimethylammonium bromide in chloroform with aqueous sodium hydroxide for 2 hr at 55° gave the dichlorocyclopropylcarbinol IIa[3] in 92% yield without appreciable deoxygenation[4] or chlorination.[5] Similarly, trisubstituted allyl alcohols, Ib, Ic,[6] and Id[6] afforded the corresponding dichlorocyclopropylcarbinols IIb[7] (74%), IIc[7] (79%), and IId[7] (60%).

Dichlorocarbene generated by the conventional methods discriminates between olefins and reacts regioselectively,[8] while that generated by the phase-transfer method has been believed to be too reactive to be selective.[2] We have found that the choice of surfactant markedly affects the regioselectivity of the adduct.[9] Thus, the allyl alcohol Ie was subjected to the dichlorocarbene addition by means of benzyldimethyl-β-hydroxyethylammonium hydroxide as a catalyst to give cyclopropylmethyl alcohol IIe[7] (selective addition of dichlorocarbene to the trisubstituted double bond) in 57% yield.

The dichlorocyclopropylcarbinols were then transformed to 2-cyclopentenones. The process involves acid-catalyzed ring opening followed by cyclization to produce the 2-cyclopentenone derivatives, all in a single operation. Treatment of alcohol IIa with 47% hydro-

(1) R. A. Ellison, *Synthesis*, 397 (1973); B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **95**, 5311 (1973), and its footnotes 19, 20, 21, and 22.

(2) G. C. Joshi, N. Singh, and L. M. Pande, *Tetrahedron Lett.*, 1461 (1972); J. Dockx, *Synthesis*, 441 (1973).

(3) D. Seyferth and V. A. Mai, *J. Amer. Chem. Soc.*, **92**, 7412 (1970).

(4) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, p 429.

(5) I. Tabushi, Z. Yoshida, and N. Takahashi, *J. Amer. Chem. Soc.*, **93**, 1820 (1971).

(6) Prepared from the corresponding methyl ketones by the action of Wadsworth–Emmons reagent and the subsequent lithium aluminum hydride reduction. *E*-Isomers of >90% purity were used.

(7) The compound gave satisfactory elemental analysis and/or parent peak in its exact mass spectrum and consistent spectral data.

(8) (a) Reference 4, p 296; (b) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965); (c) D. Seyferth and J. M. Burlitch, *ibid.*, **86**, 2730 (1964); (d) P. Weyerstahl, D. Klamann, M. Fligge, C. Finger, F. Nerdel, and J. Buddrus, *Justus Liebigs Ann. Chem.*, **710**, 17 (1967).

(9) For example, *dl*-limonene gave bis adduct when cetyltrimethylammonium bromide was used (see ref 2), while catalysis by means of benzyldimethyl-β-hydroxyethylammonium hydroxide controlled the reaction at the stage of monoaddition. Details of the reaction will be published elsewhere.