

geometry of **13** is much more conducive to formation of the C3–C7 bond than is that of **12**; in **15**, the orbitals are close and properly oriented for the final bond-forming step to give **11**. If the reaction is stepwise as depicted, **10c** would be expected to react more slowly than **10a** or **10b** because in it C5 is secondary rather than tertiary.^{14,15}

Our results suggest that it is important to consider multistep mechanisms for intramolecular [$\pi 2 + \pi 2$] cycloadditions if the substrate also contains a di- π -methane moiety.¹⁶

Acknowledgment. We thank the National Science Foundation for financial support of this work.

(14) The scheme can also be analyzed as a sequence of concerted processes. If **14** is a discrete intermediate, inversion must occur at C5. Inversion is facilitated by electron-donating or delocalizing substituents ($\text{CH}_3 > \text{H}$). We believe this is a general phenomenon with broad implications for photochemistry but reserve discussion for the full paper.

(15) For papers dealing with the sensitivity of the di- π -methane reaction to substitution at the central carbon, see H. E. Zimmerman and J. A. Pincock, *J. Amer. Chem. Soc.*, **94**, 6208 (1972); **95**, 2957 (1973); H. E. Zimmerman, R. J. Boettcher, and W. Bray, *ibid.*, **95**, 2155 (1973). The example found by Zimmerman and Pincock (formation of a bicyclo[2.1.0]pentane from a 1,4-pentadiene) is easily recognized as a "false" [$\pi 2 + \pi 2$] cycloaddition from the substitution pattern and should not be confused with the types of examples we discuss here.

(16) For other possible examples, see A. A. Gorman and J. B. Sheridan, *Tetrahedron Lett.*, 2569 (1969); G. Linstrumelle, *ibid.*, 85 (1970); A. R. Brember, A. A. Gorman, and J. B. Sheridan, *ibid.*, 481 (1973).

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Received March 23, 1974

Cyclopropanes. XXXV. The Stereochemistry of the 1-Isocyano-2,2-diphenylcyclopropyl Anion¹

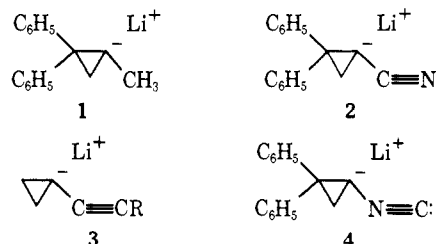
Sir:

The reaction of (–)-(R)-1-cyano-2,2-diphenylcyclopropane with lithium diisopropylamide at -60° , in ether, resulted in the formation of 1-lithio-1-cyano-2,2-diphenylcyclopropane (**2**). Subsequent alkylation with methyl iodide yielded (±)-1-methyl-1-cyano-2,2-diphenylcyclopropane.² The inference from this datum

(1) The support of this work by a grant from Hoffmann-La Roche, Inc., and a Public Health Service grant (No. 04065) from the National Cancer Institute is gratefully acknowledged.

(2) H. M. Walborsky and F. M. Hornyak, *J. Amer. Chem. Soc.*, **77**, 6026 (1955).

was that in aprotic solvents the lithium cyclopropyl ion pair was incapable of maintaining its configuration. Since under comparable conditions optically active 1-lithio-1-methyl-2,2-diphenylcyclopropane (**1**) was shown to completely maintain its configuration,³ the effect of the cyano group is to lower the barrier to inversion, presumably through delocalization. A similar result obtains when an acetylene, **3**, replaces the cyano group.⁴ Both of these groups are attached to the cyclopropyl ring by an sp-hybridized carbon atom. We wish to report our results on the configurational stability of 1-lithio-1-isocyano-2,2-diphenylcyclopropane (**4**). Here,



the isocyano function is directly attached to the ring by an sp-hybridized nitrogen atom.

The preparation of (±)- and (+)-2,2-diphenylcyclopropyl isocyanide from (±)- and (+)-2,2-diphenylcyclopropanecarboxylic acid was accomplished using a recently reported procedure.⁵ The absolute configuration of (+)-2,2-diphenylcyclopropyl isocyanide was assigned as *S* based on its chemical correlation with (+)-(*S*)-2,2-diphenylcyclopropanecarboxylic acid.⁶ The assignment of the *S* configuration to (+)-1-methyl-2,2-diphenylcyclopropyl isocyanide was made in a similar manner.⁵

In a typical experiment, a tetrahydrofuran solution of lithium diisopropylamide (6 mmol) kept under nitrogen atmosphere was cooled to -72° and a 5 ml solution of 220 mg (1 mmol) of (+)-(*S*)-2,2-diphenylcyclopropyl isocyanide was added over a 10-min period. The reaction mixture was stirred for 30 minutes and then 1.5 g (10 mmol) of methyl iodide in 5 ml of tetrahydrofuran was added over a 10-min period. The reaction mixture was allowed to warm to ambient temperature and then poured onto ice water. The ether extract was dried and stripped and the crude product was purified by column chromatography (neutral alumina) to yield 224 mg (96%) of (+)-(*S*)-1-methyl-2,2-diphenylcyclopropyl isocyanide, mp $147-51^\circ$, optical purity 98%. Table I summarizes the results of a number of alkylations performed in an identical manner but varying the temperature.

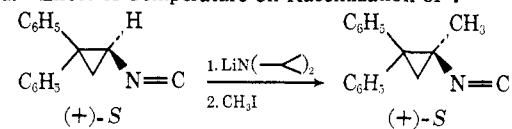
The high degree of retention of configuration of the isocyanocarbanion **4** at temperatures between -52 to -72° is surprising and contrasts dramatically with the results of the cyanocarbanion **2**. It suggests that the cyano group has a greater propensity for delocalizing an adjacent negative charge than does the isocyano group and that the isocyano group operates largely through an inductive effect. Resonance delocalization such as

(3) H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 2383 (1964).

(4) G. Kobrich, D. Merkel, and K. Imkampe, *Chem. Ber.*, **106**, 2017 (1973).

(5) H. M. Walborsky and G. E. Niznik, *J. Org. Chem.*, **37**, 187 (1972).

(6) H. M. Walborsky and C. G. Pitt, *J. Amer. Chem. Soc.*, **84**, 4831 (1962).

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 $[\alpha]_D^{25} 353 \pm 2^\circ$ (*c* 0.43, CHCl_3); optically pure 1-methyl-2,2-diphenylcyclopropyl isocyanide has $[\alpha]_D^{25} 166 \pm 1^\circ$ (*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 isocyanide 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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Received March 18, 1974

Kinetic Acidity of Cubane¹

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 $\text{p}K_A$ 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 general² 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

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

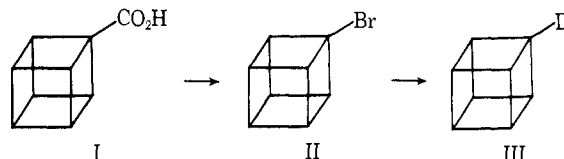
(2) (a) A. I. Shatenstein, *Advan. Phys. Org. Chem.*, **1**, 155 (1963); (b) A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, **3**, 41 (1965); (c) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965; (d) H. Fischer and D. Rewicki, *Progr. Org. Chem.*, **7**, 116 (1968); (e) D. J. Cram, *Surv. Progr. Chem.*, **4**, 45 (1968); (f) H. F. Ebel, *Fortschritt. 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.

(3) (a) A. Streitwieser, Jr., W. R. Young, and R. A. Caldwell, *J. Amer. Chem. Soc.*, **91**, 529 (1969); (b) G. L. Closs and R. B. Larrabee, *Tetrahedron Lett.*, 287 (1965); (c) R. B. Larrabee, Ph.D. Dissertation, University of Chicago, 1967; (d) D. E. Mueller, Ph.D. Dissertation, University of Chicago, 1968.

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

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 ⁶ <i>k</i> 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- <i>d</i>		2.3 ± 0.1 (2) ^c
Toluene- <i>α-d</i>		23 ± 1.0 (3) ^c
Toluene-4- <i>d</i>		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 10³ more acidic than cyclopropane, about 10⁶ more acidic than cyclobutane, and 10⁸ more acidic than cyclohexane. The large difference between cyclopropane and cyclohexane has been identified with the

(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).