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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(8) A. Streitwieser, Jr., and R. G. Lawler, *J. Amer. Chem. Soc.*, **85**, 2854 (1963); **87**, 5388 (1965).

(9) T. W. Cole, Jr., Ph.D. Dissertation, University of Chicago 1966.

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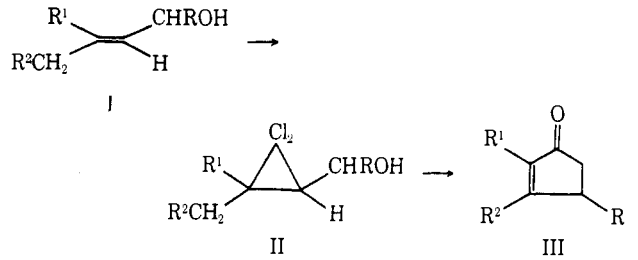
Acid-Catalyzed Reaction of Dichlorocyclopropylcarbinols. Preparation of 2-Cyclopentenones

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

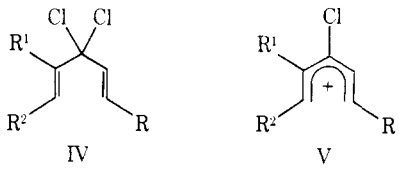
(7) The compound gave satisfactory elemental analysis and/or parent peak in its exact mass spectrum and consistent spectral data.

(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.

bromic acid at 100° for 2 hr, followed by work-up, gave 3,5-dimethyl-2-cyclopentenone[10] in 83% yield. In a similar manner IIb was converted to 2-methyl-2-cyclopentenone (IIIb)[11] in 44% yield. When IIc was exposed to this acidic condition, the resulting product proved to be 3-butyl-2-methyl-2-cyclopentenone (IIIc)[7,12] (56% yield), and none of the corresponding position isomer, 2-amyl-2-cyclopentenone, was detected. It should be noted that the original methyl group is not incorporated into the five membered ring and a long alkyl side chain resides at the 3-position. Accordingly dihydroisojasmone (IIId)[12] was obtained from IId (59% yield). Acid treatment of alcohol IIe resulted in the formation of 2-methyl-3-propenyl-2-cyclopentenone[7] (70% yield). Under this acidic condition the anticipated isoallethrone (IIIe) isomerized to more thermodynamically stable conjugated dienone. Finally the sequence was used to prepare 2,3-decamethylene-2-cyclopentenone (IIIf), a versatile intermediate of pyridomuscone,[13] muscone,[14] and [10]metacyclophane synthesis.[15] From 2-cyclododecylidene ethanol (If) the enone IIIf was obtained in 37% overall yield.

The mechanism of the cyclopentenone formation, which is not clear yet, can be rationalized by the following scheme. Conjugate dehydration of II gives IV,[16] which easily ionizes to yield the pentadienyl cation V. Thermal conrotatory ring closure[17] of V produces the cyclopentenyl cation. Deprotonation,[16] followed by hydrolysis of the resulting chlorodiene, produces III.[18]



A typical experiment is illustrated by the preparation of dihydroisojasmone. To a solution of 3-methyl-2-nonenol (Id) (880 mg, 5.64 mmol) and cetyltrimethylammonium bromide (50 mg) in chloroform (3 ml), aqueous sodium hydroxide (1.5 g in 1.5 ml of water) was added in 15 min under a nitrogen atmosphere at 55°. After stirring for 3 hr the mixture was neutralized with dilute hydrochloric acid and then worked up. Distillation at 120–125° (5 mm) gave the adduct IId (806 mg, 60%). Successively alcohol IId (476 mg, 2 mmol) was mixed with 47% hydrobromic acid (3 ml) and heated at 100° for 9 hr. Work-up and tlc purification (silica gel, ether–hexane (3:1), R_f = 0.7) gave dihydroisojasmone (IIId) (196 mg, 59%), bp 130° (bath temperature) (3 mm).

The present simple procedure coupled with the selective dichlorocarbene addition possesses wide applicability. Extention of this reaction is being explored.

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(10) The primary product may be the isomer IIIa, which is, however, recorded to isomerize to the obtained compounds under acidic conditions: I. N. Nazarov and A. N. Elizarova, *Otd. Khim. Nauk*, 295 (1951); *Chem. Abstr.*, **46**, 914*h* (1952).

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(13) K. Biemann, G. Büchi, and B. H. Walker, *J. Amer. Chem. Soc.*, **79**, 5558 (1957).

(14) G. Ohloff, J. Becker, and K. H. Schulte-Elte, *Helv. Chim. Acta*, **50**, 705 (1967); A. Eschenmoser, D. Felix, and G. Ohloff, *ibid.*, **50**, 708 (1967); D. Felix, J. Schreiber, G. Ohloff, and A. Eschenmoser, *ibid.*, **54**, 2896 (1971).

(15) S. Fujita, S. Hirano, and H. Nozaki, *Tetrahedron Lett.*, 403 (1972); S. Hirano, T. Hiyama, S. Fujita, and H. Nozaki, *Chem. Lett.*, 707 (1972).

(16) The olefin formation may be directed so that the more substituted olefin is formed.

(17) As to the cyclization of pentadienyl cation, see R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 58; P. H. Campbell, N. W. K. Chiu, K. Deugau, I. J. Miller, and T. S. Sorensen, *J. Amer. Chem. Soc.*, **91**, 6404 (1969).

(18) When the reaction of cyclopropylcarbinols with acid was performed under more mild conditions (room temperature, shorter reaction time), dehydration occurred actually under negligible formation of cyclopentenones probably due to insufficient hydrolysis of the intermediates. Attempts to isolate and identify the observed nonpolar byproducts have failed.

Structure of Bacteriochlorophyll b[1]

Sir:

Bacteriochlorophyll b (Bchl b)[2] is the principal green pigment of the photosynthetic bacterium *Rhodopseudomonas viridis*.[3] The electron excitation spectrum of Bchl b is similar to but even more strongly red shifted than that of the bacteriochlorophyll a (Bchl a), **1**. It enables this bacterium to use light down to 9800 cm^{-1} (1020 nm), the least energetic light used by any known photosynthetic organism. The close structural relationship between Bchl a and b was established by Brockmann and Kleber,[4] who converted both to 2-desvinyl-2-acetylpyromethylpheophorbide a[5] and established Mg as the central metal and phytol as the esterifying alcohol. The most distinct difference between Bchl a and b is the easy conversion of the latter into products related to chlorophyll a (Chl a), which corresponds formally to oxidation of the macrocycle from the tetrahydro- to the dihydroporphyrin level. As cis chlorins are easily oxidized to porphyrins and show a red-shifted visible absorption spectrum compared to the corresponding trans epimers,[6] Brockmann[4] in 1970 formulated Bchl b as the 3,4-cis epimer of Bchl a (structure **2**).

At the end of the same year, Baumgarten[7] proposed structure **3** for Bchl b, which formulates Bchl b as the Δ4,4a isomer of Chl a. The red shift in the electron excitation spectrum is explained by the α,β unsaturation of the Bchl a chromophore,[8] and the easy "oxida-

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) K. E. Eimhjellen, O. Aasmundrud, and A. Jensen, *Biochem. Biophys. Res. Commun.*, **10**, 232 (1963).

(3) G. Drews and P. Giesbrecht, *Arch. Mikrobiol.*, **53**, 255 (1966); N. Pfennig and H. G. Trueper, *Int. J. Syst. Bacteriol.*, **21**, 19 (1971).

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(5) H. H. Inhoffen, P. Jaeger, R. Maehlhop, and C. D. Mengler, *Justus Liebigs Ann. Chem.*, **704**, 188 (1967).

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(8) In a similar manner, the Δ2,2a and Δ4,4a isomers of porphyrins exhibit a chlorin spectrum; *cf.* H. H. Inhoffen, H. Brockmann, Jr., and K. Bliesener, *Justus Liebigs Ann. Chem.*, 730, 173 (1969).