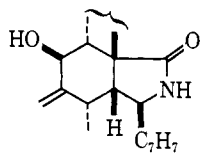
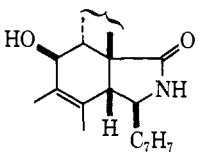
The Ag to O distances are 2.72 (O(40)) and 2.98 Å (O(39)). The closest approach between the toxin and the Ag is the 2.42 Å distance to O(21). The distance from the water of crystallization (O(41)) to the Ag is 2.61 Å and between O(41) and O(33) of the toxin the distance is 3.01 Å. The coordination about Ag is approximately octahedral. There are no other abnormally short intermolecular contacts in the crystal structure.[14]

After these studies had been completed identity of the toxin with cytochalasin E[6] was established by comparison of melting point and mixture melting point, ir and mass spectra, and optical rotations.[15] The previously proposed structure of cytochalasin E therefore



D



E

is incorrect and has to be replaced by **1**. Acid-catalyzed isomerization to compounds with part structures D and E is now unexceptional. By analogy cytochalasin F[6] has structure **2**.

Cytochalasin E killed rats within a few hours after dosing, the LD_{50} value being 2.6 or 9.1 mg/kg body weight after intraperitoneal or oral administration of a single dose. Death was due to circulatory collapse caused by massive extravascular effusion of plasma.

Acknowledgment. The work at Massachusetts Institute of Technology was supported by the National Cancer Institute (Contract No. NCl-E-73-3217).

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-5423.

(14) See paragraph at end of paper regarding supplementary material.
(15) We are indebted to Dr. W. B. Turner for a sample of cytochalasin E.
(16) Camille and Henry Dreyfus Foundation Teacher–Scholar Grant Awardee, 1972–1977, and Fellow of the Alfred P. Sloan Foundation, 1973–1975.

George Büchi,* Yoshihiko Kitaura, Sun-Shine Yuan
Department of Chemistry, Massachusetts Institute of Technology Cambridge, Massachusetts 02139

Hal E. Wright, Jon Clardy*[16]
Ames Laboratory—U. S. Atomic Energy Commission and Iowa State University Ames, Iowa 50010

Arnold L. Demain, Thirayudh Glinsukon Nadine Hunt, Gerald N. Wogan
Department of Nutrition and Food Science Massachusetts Institute of Technology Cambridge, Massachusetts 02139

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Chromic Acid Oxidation of Cyclopropanols

Sir:

In all previously investigated chromic acid oxidations of secondary alcohols, the chromium(VI) oxidation step yields the corresponding ketone.[1] The rate-limiting step in these oxidations is the breaking of the α-carbon–hydrogen bond. Strained alcohols, like cyclobutanol or 7-norbornanol, form no exception to this rule,[2,3] although they are very prone to undergo a ring-opening reaction under carbon–carbon bond cleavage with one-electron oxidants like chromium(IV),[2] cerium(IV),[4] vanadium(V),[5] or manganese(III).[5]

In this communication we wish to report the strikingly different behavior of cyclopropanols.[6] We have found that cyclopropanol reacts with chromic acid about 2000 times faster than typical secondary alcohols (Table I) to yield β-hydroxypropionaldehyde.[7,8]

The oxidation product of 1-phenylcyclopropanol, β-hydroxyethyl phenyl ketone, isolated directly by extraction and column chromotography accounted for 73% of the isolated product (43% yield): ir (CCl_4) 3480 (broad), 1680 cm^{-1}; nmr (CCl_4) δ 7.90 (m, 2), 7.44 (m, 3), 3.90 (t, J = 5 Hz, 2), 3.10 (t, J = 5 Hz, 2), and 2.54 (s, 1); mass spectrum (70 eV) m/e 132 ($P - H_2O$), 105, 77.

The cyclopropane ring itself is rather unreactive toward chromic acid, as is clearly indicated by the low reactivity of cyclopropylcarbinol, methyl cyclopropyl ether, and 1,2,2-trimethylcyclopropyl acetate.

Tertiary cyclopropanols are more reactive than the corresponding secondary cyclopropanols. This enhanced reactivity is in sharp contrast with the very low reactivity of other[9,10] tertiary alcohols.[11–13]

The reactivity of both secondary and tertiary cyclopropanols is greatly increased by substitution in the ring; 1,2,2,3,3-pentamethylcyclopropanol is about 6×10^6 times more reactive than isopropyl alcohol and is, with respect to chromic acid oxidation, the most reactive organic compound known.

The mechanism of the reaction can best be understood in terms of a rate-limiting oxidative decomposition of a chromic acid ester of the alcohol (Scheme I). The driving force for the reaction is the relief of the

(1) For a review of this subject, see K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965.
(2) J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, **90**, 2987 (1968).
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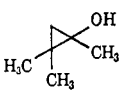
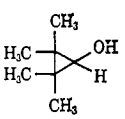
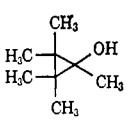
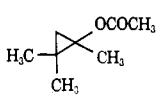
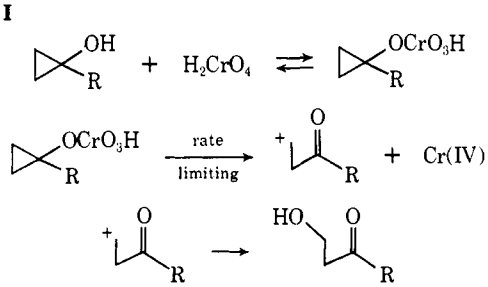
(8) R. H. Hall and E. S. Stern, *J. Chem. Soc.*, 490 (1950).
(9) The observation[10] that chromium(VI) oxidizes triphenylcarbinol faster than diphenylcarbinol in highly acidic media (but not at lower acid concentrations) represents the only previously recorded exception to this rule.
(10) R. Stewart and F. Banoo, *Can. J. Chem.*, **47**, 3207 (1969).
(11) J. Roček and A. Radkowsky, *Tetrahedron Lett.*, 2835 (1968).
(12) W. F. Sager, *J. Amer. Chem. Soc.*, **78**, 4970 (1956).
(13) J. Roček, *Collect. Czech. Chem. Commun.*, **23**, 833 (1958).

Table I. Chromic Acid Oxidation Rates[a] of Cyclopropanols and Related Compounds at 25°

Substrate	k, M^{-1} sec^{-1}	k_{rel}
pH 1.2 (6.2×10^{-2} M $HClO_4$)		
	0.36	1.0
	2.3	6.4
	0.74	2.1
	$\leq 10^{-5}$	$\leq 3 \times 10^{-5}$
$(CH_3)_2CHOH$	0.69×10^{-4}	1.9×10^{-4}
	1.93×10^{-4}	5.4×10^{-4}
	1.41×10^{-4}	3.9×10^{-4}
	1.83×10^{-4}	5.1×10^{-4}
pH 3.1 (CH_3CO_2H–CH_3CO_2Na buffer)		
	1.42×10^{-2}	1.0
	2.20×10^{-2}	1.6
	11.1	780
	8.2	570
	15.9	1120
	0	0

[a] Rates were determined spectrophotometrically at the absorption maximum for chromic acid (350 nm) under pseudo-first-order conditioning. All alcohols give good straight line plots.

Scheme I



ring strain. The reaction is further accelerated by substituents stabilizing the incipient carbonium ion[14] and carbonyl group.

(14) We assume that the formation of the carbon–oxygen bond occurs at least to some extent synchronously with the ring cleavage reaction. However, the strong rate-accelerating effect of β substituents indicates that a positive charge does develop on the β-carbon in the transition state of the oxidative decomposition.

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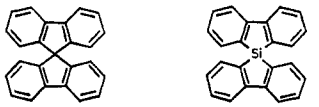
(15) Work done at The Catholic University of America, Washington, D. C.

Jan Roček,* Alberto M. Martinez, George E. Cushmac[15]
Department of Chemistry, University of Illinois at Chicago Circle
Chicago, Illinois 60680
Received April 19, 1973

A Quantitative Account of Spiroconjugation[1]

Sir:

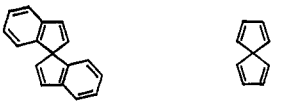
Recently we were able to detect spiroconjugation[2,3] by photoelectron spectroscopy in the symmetric spirans 9,9′-spirobifluorene (**1**)[4] and 9,9′-spirobi(9-silafluorene) (**2**)[4] and the nonspiro compounds tetravinylmethane (**3**)[5] and tetravinylsilane (**4**).[5,6] Here we report the



(1) (2)

$C(CH=CH_2)_4$ $Si(CH=CH_2)_4$

(3) (4)



(5) (6)

detection of spiroconjugation in the newly synthesized[7,8] dissymmetric spiran 1,1′-spirobiindene (**5**) and present a linear correlation between measured and calculated spiro splittings.

Figure 1 shows a section of the photoelectron (pe) spectrum of **5**. In the corresponding range, the pe spectrum[9] of indene exhibits three bands which were assigned to ionizations from the highest three π molecular orbitals (MO's) (π_1 = 8.13 eV, π_2 = 8.95, and π_3 = 10.29). The comparison of both spectra reveals that each of the three bands in the spectrum of indene is split into two bands (π_1 = 7.80 eV, π_2 = 8.37, splitting

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(3) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967).
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(5) A. Schweig, U. Weidner, J. G. Berger, and W. Grahn, *Tetrahedron Lett.*, 557 (1973).
(6) U. Weidner and A. Schweig, *Angew. Chem.*, **84**, 551 (1972); *Angew. Chem. Int. Ed. Engl.*, **11**, 537 (1972).
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