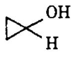
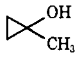
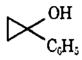
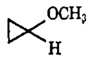
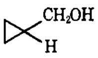
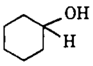
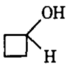
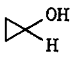
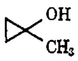
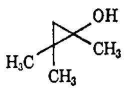
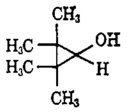
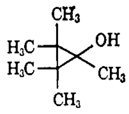
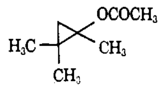
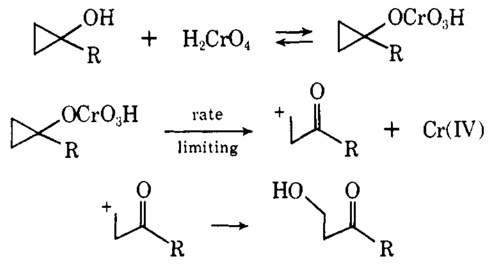
Table I. Chromic Acid Oxidation Rates[a] of Cyclopropanols and Related Compounds at 25°

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.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the National Science Foundation, and to the U. S. Army Research Office, Durham, N. C., for generous support of this research.

[15] Work done at The Catholic University of America, Washington, D. C.

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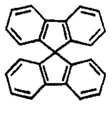
Received April 19, 1973

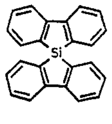
A Quantitative Account of Spiroconjugation[1]

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 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.



(1)



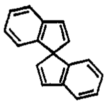
(2)

$C(CH{=}CH_2)_4$

(3)

$Si(CH{=}CH_2)_4$

(4)



(5)

(6)

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

[1] Part 36 of "Theory and Application of Photoelectron Spectroscopy;" part 35: W. Schäfer, A. Schweig, G. Märkl, and H. Heier, submitted for publication.

[2] H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967).

[3] R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967).

[4] A. Schweig, U. Weidner, D. Hellwinkel, and W. Krapp, *Angew. Chem.*, **85**, 360 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 310 (1973).

[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).

[7] R. K. Hill and D. A. Cullison, *J. Amer. Chem. Soc.*, **95**, 1229 (1973).

[8] J. H. Brewster and R. T. Prudence, *ibid.*, **95**, 1217 (1973).

[9] J. H. D. Eland and C. J. Danby, *Z. Naturforsch. A*, **23**, 355 (1968).

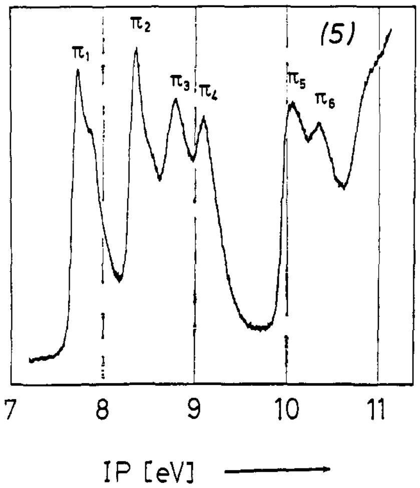
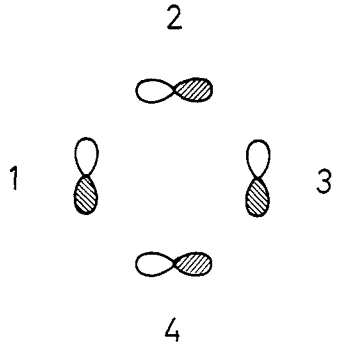


Figure 1. Section of the photoelectron spectrum of 1,1′-spirobiindene (5). The He–I (584 Å) photoelectron spectra were measured on a PS-18 spectrometer from Perkin-Elmer Ltd., Beaconsfield (England).

= 0.57; π_3 = 8.80, π_4 = 9.10, splitting = 0.30; π_5 = 10.20, π_6 = 10.48, splitting = 0.28) in the spectrum of the corresponding spiran **5**.

The spiro splitting ΔE (relying on degenerate first-order perturbation theory and considering only interactions (β) between the atomic orbitals (AO's) 1 to 4 next to the tetrahedral atom with coefficients c_1 to c_4 in



the unperturbed systems) is given as[2]

$$\Delta E = 2(c_1c_2 - c_1c_4 - c_2c_3 + c_3c_4)\beta \qquad (1)$$

Plotting the measured spiro splittings ΔE in the series of carbon compounds (**1** = 0.30,[4] **5** = 0.57, **3** = 0.73, and spiro[4.4]nonatetraene (**6**) = 1.23 eV[10]) against the values derived from the expression ($c_1c_2 - c_1c_4 - c_2c_3 + c_3c_4$) (**1** = 0.46, **5** = 0.59, **3** = 0.88, and **6** = 1.25)[11] gives a straight line (Figure 2) which passes through the origin. The slope of this line yields β = 0.49 ± 0.05 eV.

With β known eq 1 can now be used to predict spiro splittings. Accordingly the splittings expected for the lower MO's π_2 and π_3 in indene, 0.22 and 0.25 eV, respectively, are in good agreement with the observed ones.

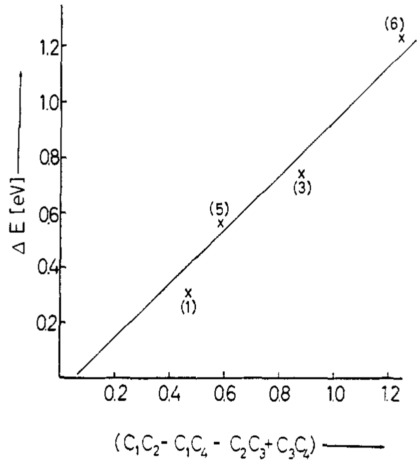


Figure 2. Correlation between the measured spiro splittings ΔE (ordinates) and the values derived from the expression ($c_1c_2 - c_1c_4 - c_2c_3 + c_3c_4$) (abscissa).

Acknowledgments. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie; in addition, grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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Received May 31, 1973

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(10) E. Heilbronner, personal communication.

(11) Coefficients obtained by the MINDO/2 method[12] are used throughout.

(12) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

Concerning the Stereochemistry of Reduction of Cyclohexanones with Complex Metal Hydrides

Sir:

One of the most fundamental reactions in organic chemistry is the reduction of a ketone to an alcohol using $LiAlH_4$ in ether solvent. In spite of the widespread use and fundamental nature of this reaction, little is known about the mechanism. Although there has been speculation[1] concerning the role of lithium in the reaction, it has only recently been demonstrated that a ketone will associate with a lithium cation in tetrahydrofuran.[2] Even if a complex is observed when $LiAlH_4$ is added to a ketone, it would not prove that the reaction is occurring *via* a complex. For example, when 4-*tert*-butylcyclohexanone is allowed to react with $Al(CH_3)_3$ in a 1:1 ratio in benzene, a complex is formed involving an aluminum–oxygen bond yet the product is not formed directly from the complex.[3] When the ratio is 1:2 a second molecule of $Al(CH_3)_3$ attacks the complex giving very different stereochemical results than when the ratio of reactants is 1:1. Eliel[4] and coworkers have reported

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(1) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Menlo Park, Calif., 1972, p 49 ff.

(2) Frank R. Dobbs, Ph.D. Thesis, 1972, Georgia Institute of Technology, Atlanta, Ga.

(3) (a) H. M. Neumann, J. Laemmle, and E. C. Ashby, *J. Amer. Chem. Soc.*, **95**, 2597 (1973); (b) J. Laemmle, E. C. Ashby, and P. V. Roling, *J. Org. Chem.*, **38**, 2526 (1973).

(4) (a) E. L. Eliel and Y. Senda, *Tetrahedron*, **26**, 2411 (1970); (b) J. Klein, E. Durkelblum, E. L. Eliel, and Y. Senda, *Tetrahedron Lett.*, 6127 (1968).