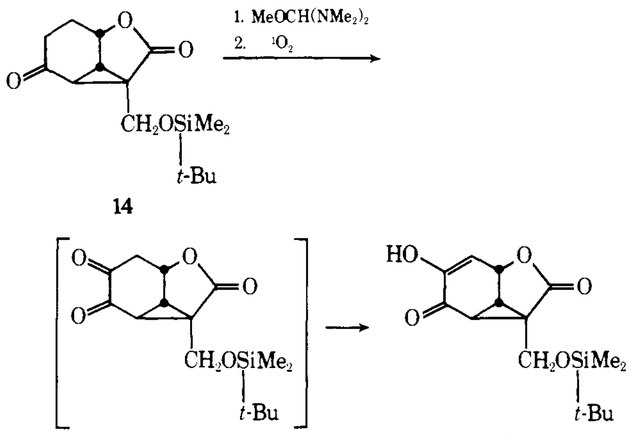

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The experimental procedure for the conversion of menthone **2** to buchu-camphor (**8**) is representative of the oxidation conditions employed. A mixture of 1.10 g (7.13 mmol) of freshly distilled menthone (**2**) and 1.50 g (8.60 mmol) of *tert*-butoxybis(dimethylamino)methane was heated with stirring under nitrogen at 55 °C for 24 h. The resulting crude enamino ketone was dissolved in 150 ml of methylene chloride and photooxygenated at −78 °C using a constantly circulating oxygen supply with bisacenapthalenethiophene (5 mg) as a sensitizer, and a Sylvania DWY 650-W lamp as a light source. After the uptake of oxygen ceased (45 min, 1.2 equiv of oxygen), the irradiation was stopped and the reaction mixture was allowed to warm slowly to room temperature. The solution was concentrated and the residue was immediately extracted with 150 ml of ether. The ether solution was washed repeatedly with cold water, dried with magnesium sulfate, and stirred over activated charcoal. The resulting solution was filtered through Celite, concentrated, and dried under vacuum to give 0.97 g (81% overall from **2**) of buchu-camphor (**8**), mp 82–83 °C (lit.[17] 83–84 °C).[18]

We are continuing to investigate synthetic applications of this method.

Acknowledgment. We are grateful to the National Institutes of Health, Grant GM-13854, for financial support.

References and Notes

(1) Dedicated to Professor R. B. Woodward on the occasion of his 60th birthday.

(2) Notable examples of the involvement of this transformation in key synthetic steps are found in the synthesis of colchicine, strychnine, and other natural products: R. B. Woodward, *Harvey Lect.*, 31 (1964); R. B. Woodward, M. P. Cava, W. D. Ollis, A. Hunger, H. U. Doeniker, and K. Schenker, *Tetrahedron*, **19**, 247 (1963); G. Buchi, W. D. MacLeod, and J. Padilla, *J. Am. Chem. Soc.*, **86**, 4438 (1964); S. Kagawa, S. Matsumoto, S. Nishida, S. Yu, J. Morita, A. Ichihara, H. Shirahama, and T. Matsumoto, *Tetrahedron Lett.*, 3913 (1969).

(3) (a) N. Rabjohn, *Org. React.*, **5**, 331 (1949); (b) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. I, Wiley, New York, N.Y., 1967, p 40.

(4) N. Kornblum and H. W. Frazier, *J. Am. Chem. Soc.*, **88**, 865 (1966).

(5) H. Brederick, F. Effenberger, and G. Simchen, *Chem. Ber.*, **96**, 1350 (1963); *ibid.*, **98**, 1078 (1965); H. Brederick, G. Simchen, S. Rebsdat, W. Katlehner, P. Horn, R. Wahl, H. Hoffmann, and P. Grieshaber, *ibid.*, **101**, 41 (1968).

(6) The reagent has beem employed recently in the synthesis of enamino ketones of spirocyclobutanones: B. M. Trost and M. Preckel, *J. Am. Chem. Soc.*, **95**, 7862 (1973); B. M. Trost, M. Preckel, and L. M. Leichter, *ibid.*, **97**, 2224 (1975).

(7) In the first phase of our investigation, the ketones were formylated at the α-position and then converted to the enamino ketones by reaction with secondary amines such as morpholine or diethylamine. Photooxidation of these derivatives yielded α-diketones in excellent yields. In a subsequent modification using DMF derivatives, we have isolated intermediates of type 1 prior to the singlet oxygen reaction. More recently we have found the isolation of these intermediates to be unnecessary.

(8) In early work[9,10] it was shown that the photooxygenation of aldehyde enamines leads to the rupture of the carbon–carbon double bond through intermediate dioxetanes to give amide and carbonyl fragments. On the other hand, the enamines of cyclic ketones[11] undergo reaction with singlet oxygen to yield α-oxygenated ketones. Very recently[12,13] photooxygenation of the enamines of acyclic ketones have provided mixed results—cleavage of the carbon–carbon double bond to form amide and carbonyl components, or α-oxygenation.

(9) C. S. Foote and J. W.-P. Lin, *Tetrahedron Lett.*, 3267 (1968); J. E. Huber, *ibid.*, 3271 (1968); C. S. Foote, A. A. Dzakpasu, and J. W.-P. Lin, *ibid.*, 1247 (1975).

(10) There are also many examples of the reactions of heterocyclic systems with singlet oxygen, in which enamine units appear to be involved as reactive components. Here again the same type of cleavage of a carbon–carbon double bond occurs: H. H. Wasserman, K. Stiller, and M. B. Floyd, *Tetrahedron Lett.*, 3277 (1968); T. Matsuura and I. Saito, *Tetrahedron*, **25**, 557 (1969).

(11) H. H. Wasserman and S. Terao, *Tetrahedron Lett.*, 1735 (1975).

(12) W. Ando, T. Saiki, and T. Migita, *J. Am. Chem.* * *Soc.*, **97**, 5028 (1975).

(13) H. H. Wasserman and J. L. Ives, to be submitted for publication.

(14) In an earlier report on the photooxidation of an enamino ketone, the conversion of an aminoindenone to a spiroketo lactone is described: K. Orito, R. H. Manske, and R. Rodrigo, *J. Am. Chem. Soc.*, **96**, 1944 (1974).

(15) (a) The selenium dioxide oxidation of menthone is reported to give only a low yield (15%) of buchu-camphor and higher oxidized products: H. L. Riley, J. F. Morely, N. A. C. Friend, *J. Chem. Soc.*, 1875 (1932); S. Hirayama, *J. Chem. Soc. Jpn.*, **58**, 1383 (1937); (b) The oxidation of 3-cholestanone yields only 30% of the desired 2,3-cholestandione: E. T. Stiller and O. Rosenheim, *J. Chem. Soc.*, 353 (1938).

(16) F. E. Ziegler and J. Photis, private communication.

(17) A. K. Macbeth and W. G. P. Robertson, *J. Chem. Soc.*, 3512 (1953).

(18) The use of heterogeneous sensitization (polymer-bound Rose Bengal, Photox, Hydron Laboratories, Inc.) gave identical yields of α-diketones and permitted easy separation of the product from the sensitizer.

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Nonempirical Electronegativity Scale

Sir:

Electronegativity is one of the most useful of all the qualitative concepts in chemistry. There have been many attempts to quantify this concept through the establishment of electronegativity scales such as the Pauling scale[1] (based on bond energies), the Mulliken scale[2] (based on ionization energies and electron affinities), the Allred–Rochow scale[3] (based on atomic energies and covalent radii), the Sanderson scale[4] (also based on covalent radii), the Phillips scale[5] (based on dielectric properties), and the St. John–Bloch scale[6] (based on quantum defects). All of these scales are at least partially empirical, and all are indirect in that they depend on the experimental values of properties which, in turn, depend on or monitor electronegativity. Ab initio quantum chemistry has often been successful in calculating numerical values for the observables which are required for these scales, but the less well-defined construct of electronegativity has heretofore not been directly treated. In this communication we report a nonempirical procedure for extracting electronegativities from ab initio FSGO wavefunctions. As a result, we are able to construct what is, to the best of our knowledge, the first nonempirical electronegativity scale.

The floating spherical Gaussian orbital (FSGO) method focuses directly on core, lone-pair, and bonding orbitals instead of constructing them from atomic orbitals. Since its inception by Frost,[7] the method has been well characterized.[8] Single bonds are described by Gaussian orbitals centered on, or nearly on, bond axes, while "banana" bonds are used for multiple bonds.[8] The orbitals are allowed to float to location of minimum energy. A polar single bond between atoms A and B might therefore be represented schematically as A- -X- - -B, where X denotes the center of the bond orbital. If one defines an orbital multiplier[9] f_{AB},

$$f_{\mathrm{AB}} = R_{\mathrm{A}}/(R_{\mathrm{A}} + R_{\mathrm{B}}) \qquad (1)$$

where R_{A} and R_{B} are the distances from the atoms to the orbital center, then if $f_{\mathrm{AB}} < 0.5$, atom A can be regarded[10] as attracting the bonding electrons more strongly than atom B; if $f_{\mathrm{AB}} > 0.5$, the converse is true, and if $f_{\mathrm{AB}} = 0.5$, there is equal

Table I. Electronegativities[a, b]

	Li	Be								B	C	N	O	F
H	1.00	1.48								1.84	2.35	3.16	3.52	4.00
P	0.98	1.57								2.04	2.55	3.04	3.44	3.98
A	0.97	1.47								2.01	2.50	3.07	3.50	4.10
S	0.99	1.50								2.00	2.50	3.00	3.50	4.00
	Na	Mg								Al	Si	P	S	Cl
H	0.89	1.24								1.40	1.64	2.11	2.52	2.84
P	0.93	1.31								1.61	1.90	2.19	2.58	3.16
A	1.01	1.23								1.47	1.74	2.06	2.44	2.83
S	0.91	1.18								1.43	1.66	1.90	2.12	2.35
	K	Ca	Sc	Ti	V	Cr	Mn	Cu	Zn	Ga	Ge	As	Se	Br
H	0.73	0.96	1.14	1.27	1.42	1.72	1.88	1.10	1.40	1.54	1.69	1.99	2.40	2.52
P	0.82	1.00	1.36	1.54	1.63	1.66	1.55	1.90	1.65	1.81	2.01	2.18	2.55	2.96
A	0.91	1.04	1.20	1.32	1.45	1.56	1.60	1.75	1.66	1.82	2.02	2.20	2.48	2.74
S	0.79	1.10							1.40	1.50	1.66	1.81	1.96	

[a] FSGO values are based on hydride scale: $\epsilon_{Li} = 1.00$; $\epsilon_F = 4.00$. On this scale $\epsilon_H = 2.79$ as compared with 2.20 on Pauling and Allred–Rochow scales. [b] H denotes FSGO hydride scale; P denotes Pauling scale, values from A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961); A denotes Allred–Rochow scale, values from ref 3; S denotes St. John–Bloch scale, values from ref 6.

sharing of the bonding electrons. In short, the deviation of f_{AB} from 0.5 measures the degree of electron transfer within a bond, and this is, presumably, the most conceptually attractive and most direct measure of differences in electron attracting power, or electronegativity.[11]

The simplest definition of electronegativity difference in terms of f_{AB} is a direct proportionality:[12]

$$(\epsilon_B - \epsilon_A) = K(f_{AB} - 0.5) \qquad (2)$$

the constant in eq 2 may be eliminated by taking a ratio,

$$(\epsilon_B - \epsilon_A)/(\epsilon_B - \epsilon_C) = (f_{AB} - 0.5)/(f_{CB} - 0.5) \qquad (3)$$

from which we note that if reference electronegativities are selected for two elements to set a standard point and scale expansion factor, then electronegativities can be generated for other atoms using only the f_{AB} values taken from ab initio quantum mechanical calculations. Alternatively, eq 2 could be rewritten as

$$(\epsilon_B - \epsilon_A) = K(R_A - R_B)/(2R_A + 2R_B) \qquad (4)$$

Equation 4 emphasizes the fundamental symmetry of our definition. Further, since the classical bond contribution to the molecular dipole moment would be $\delta = 2e(R_A - R_B)/2$, eq 4 displays the anticipated relationship between electronegativity and dipole moment.

Since many hydrides have been studied by the FSGO method,[13] hydrides have been used to generate a nonempirical electronegativity scale. Li and F (in LiH and HF) were assigned the electronegativities 1.00 and 4.00, respectively, and electronegativities were subsequently calculated for H and the other atoms[14] listed in Table I. One observes that the predicted electronegativities are in remarkable agreement with widely used empirical values. The small lowering of the electronegativities of most third-row elements, in comparison to the Pauling or Allred–Rochow values, is consistent with the trends suggested by Phillips[5] and St. John and Bloch.[6] With the exception of H (which is unique in the FSGO framework in that there is no nuclear shielding) and Cu (the bond length of CuH is grossly overestimated by FSGO[13d]), the agreement with the Allred–Rochow scale is particularly striking. However, in contrast to the Allred–Rochow scale, note that sulfur is predicted to be more electronegative than carbon, in agreement with chemical behavior.

We find that the proposed electronegativity scale is usually consistent with electronegativity differences (computed from f_{AB} by eq 2 or 3) for nonhydride compounds. For example (hydride scale in parenthesis): $\epsilon_{Cl} - \epsilon_{Li} = 1.80$ (1.84) in LiCl, $\epsilon_O - \epsilon_{Be} = 1.87$ (1.69) in BeO, $\epsilon_O - \epsilon_{Si} = 1.86$ (1.88) in SiO, $\epsilon_O - \epsilon_C = 1.28$ (1.17) in methanol, $\epsilon_O - \epsilon_H = 0.70$ (0.74) in methanol, and $\epsilon_{Li} - \epsilon_{Na} = 0.13$ (0.11) in NaLi. However, electronegativities vary, as one might expect, with number of lone pairs and formal charge. For example, $\epsilon_O = 3.84$, 3.74, 3.52, and 3.23 in the respective species H_4O^{2+}, H_3O^+, H_2O, and OH^-; $\epsilon_{Sc} = 1.14$ and 1.04 in ScH_3 and ScH; and $\epsilon_O - \epsilon_C = 1.54$ (1.17) in the triply bonded carbon monoxide.

In conclusion we suggest that the above results constitute prima facie evidence for both the validity of the generally accepted interpretation of electronegativity and for the conceptual utility of the FSGO method.

References and Notes

(1) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, pp 88–93.

(2) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934); **3**, 573 (1935).

(3) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).

(4) R. T. Sanderson, *J. Chem. Educ.*, **29**, 539 (1952); **31**, 2, 238 (1954).

(5) J. C. Phillips, "Covalent Bonding in Crystals, Molecules, and Polymers", University of Chicago Press, Chicago, Ill., 1969, p 230.

(6) J. St. John and A. N. Bloch, *Phys. Rev. Lett.*, **33**, 1095 (1974).

(7) A. A. Frost, *J. Chem. Phys.*, **47**, 3707 (1967).

(8) See, for example, E. R. Talaty, A. K. Schwartz, and G. Simons, *J. Am. Chem. Soc.*, **97**, 972 (1975) and references cited therein.

(9) P. H. Blustin and J. W. Linnett, *J. Chem. Soc., Faraday Trans. 2*, **70**, 274 (1974).

(10) This is an interpretation, as the location of the center of a bonding orbital is being considered instead of the molecular electron density.

(11) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(12) This definition requires a well-defined bonding orbital and may not apply to extremely ionic bonding such as in alkali fluorides.

(13) (a) First-row hydrides, A. A. Frost, *J. Phys. Chem.*, **72**, 1289 (1968); (b) second-row hydrides, S. Y. Chu and A. A. Frost, *J. Chem. Phys.*, **54**, 760 (1971); (c) K–Mn hydrides, E. R. Talaty, A. J. Feary, and G. Simons, *Theor. Chim. Acta*, **41**, 133 (1976); (d) Cu–Br hydrides, G. Simons and E. R. Talaty, unpublished.

(14) Using the calculated multipliers $f_{LiH} = 0.893$ and $f_{FH} = 0.233$ in eq 3, and setting $\epsilon_{Li} = 1.000$ and $\epsilon_F = 4.000$, yields $\epsilon_H = 2.786$ and $K = 4.546$. In methane, for example, $f_{CH} = 0.595$; hence, $\epsilon_C = -4.546(f_{CH} - 0.5) + 2.786 = 2.354$.

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Synthesis of 2-Amino-5-cyano-7-(β-D-ribofuranosyl)pyrrolo[2,3-*d*]pyrimidin-4-one. An Important Precursor for the Synthesis of Nucleoside Q and Q*

Sir:

The structure of nucleoside Q was recently elucidated and reported[1] to be 2-amino-5-(4,5-*cis*-dihydroxy-1-cyclopenten-3-yl-*trans*-aminomethyl)-7-(β-D-ribofuranosyl)pyrrolo[2,3-*d*]pyrimidin-4-one (**1a**). This modified nucleoside oc-