sorption by the cyanoferriheme (ref 7e), in fact result from a release of CN$^-$ (Q. H. Gibson, private communication). This release we attribute to a decrease in affinity for CN$^-$ upon transition from the high-affinity R state to the low-affinity T state.

(13) H. Sussner, A. Mayer, H. Brunner, and H. Fasold, *Eur. J. Biochem.*, **41**, 465 (1974).

(14) T. G. Spiro, and J. M. Burke, *J. Am. Chem. Soc.*, **98**, 5482 (1976).

(15) B. M. Hoffman, *J. Am. Chem. Soc.*, **97**, 1688 (1975).

(16) This conclusion does not apply to Hb(NO), (see A. Szabo and L. D. Barron, *J. Am. Chem. Soc.*, **97**, 660 (1975)), which has substantially different properties due to the strong trans effect of NO. See ref 3e.

(17) As a further probe of porphyrin properties, epr measurements have been initiated.

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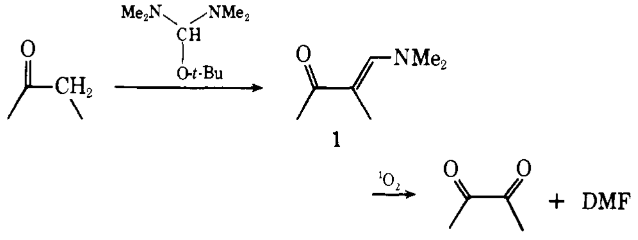
A Novel Method for Converting Ketones to α-Diketones. The Reaction of Enamino Ketones with Singlet Oxygen[1]

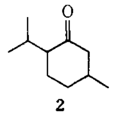
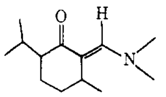
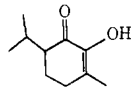
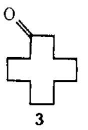
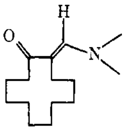
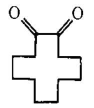
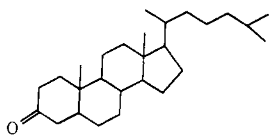
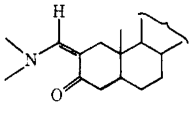
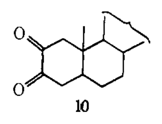
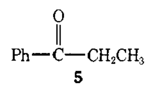
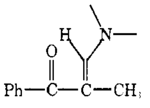
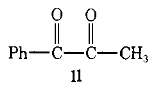
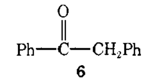
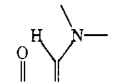
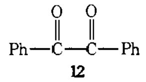
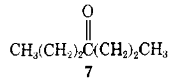
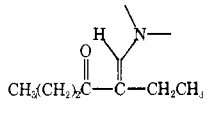
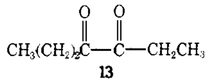
Sir:

The oxidation of a methylene group α to a ketone to form an α-diketone is an important functional group transformation which has many applications in organic synthesis.[2] Conventional reagents for accomplishing this transformation, including selenium dioxide[3a] or alkyl nitrites in acid or base,[3b] often lead to further oxidation or side reactions because of the strong reaction conditions employed. Other methods involving α-halogenation or α-oxygenation followed by further oxidation,[4] or α-formylation followed by dithiane formation and hydrolysis[2] may be limited to special systems.

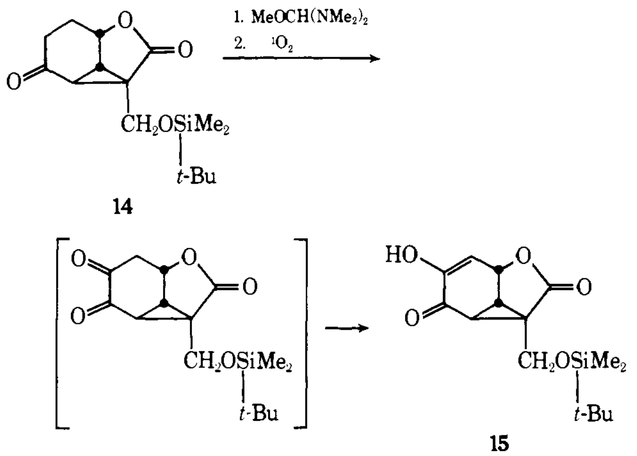


We now report a new method for conversion of a ketone to an α-diketone, which is generally applicable and *mild enough to use on complex systems containing sensitive functional groups.* The procedure consists of the transformation of the ketone to the enamino ketone (**1**) by reaction with an alkoxybis(dimethylamino)methane (a reactive derivative of DMF)[5,6] followed by cleavage of the carbon-carbon double bond using singlet oxygen.[7-14] The fact that one does not need to isolate the intermediate (**1**) lends simplicity to the method, as outlined below. Table I lists the ketones oxidized, reaction conditions, and products. The high yields in the conversion of menthone (**2**) and cholestanone (**4**) to the corresponding diones **8** and **10** may be contrasted with the reported poor results in the use of selenium dioxide.[15] Of particular interest is the oxidation of ketone **14**, an intermediate in a current natural product synthesis.[16] Conversion of **14** to **15** took place in 85% yield under the conditions outlined below despite the presence in the molecule of several sensitive functional groups in a strained tricyclic system.

Table I. Conversion of Ketones to Diketones

Ketone		Enamino ketone[c]		α-Diketone[d]	Overall yield, %
 **2**	$\xrightarrow[55\ °C,\ 24\ h]{a}$		$\xrightarrow{b}$	 **8**	81
 **3**	$\xrightarrow[60\ °C,\ 24\ h]{a}$		$\xrightarrow{b}$	 **9**	82
 **4**	$\xrightarrow[55\ °C,\ 18\ h]{a}$		$\xrightarrow{b}$	 **10**	87
 $Ph-C(=O)-CH_2CH_3$ **5**	$\xrightarrow[65\ °C,\ 18\ h]{a}$		$\xrightarrow{b}$	 $Ph-C(=O)-C(=O)-CH_3$ **11**	68
 $Ph-C(=O)-CH_2Ph$ **6**	$\xrightarrow[55\ °C,\ 3\ h]{a}$		$\xrightarrow{b}$	 $Ph-C(=O)-C(=O)-Ph$ **12**	89
 $CH_3(CH_2)_2C(=O)(CH_2)_2CH_3$ **7**	$\xrightarrow[55\ °C,\ 24\ h]{a}$		$\xrightarrow{b}$	 $CH_3(CH_2)_2C(=O)-C(=O)-CH_2CH_3$ **13**	74

[a] Reaction of the ketone with a slight excess of *tert*-butoxybis(dimethylamino)methane. Reaction times were determined by the disappearance of the IR carbonyl absorption of the starting ketone. [b] Photooxygenation of the enamino ketone in methylene chloride at −78 °C using 3–5 mg of bisacenapthalenethiophene and a Sylvania DWY 650-W lamp (workup involved repeated washing with water, drying, removal of the sensitizer with charcoal, filtering, concentrating, and drying in vacuo to give pure α-diketone). [c] All enamino ketones have been isolated, characterized, and photooxygenated to give the same products as those formed in the one-step conversion described. [d] All α-diketones were identified by IR, NMR, comparison with authentic material, and/or elemental analysis.



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