after stirring 5 min the mixture was washed with 1 *N* HCl and $NaHCO_3$ solution, dried, and evaporated. The residue was dissolved in benzene, filtered to remove some dicyclohexylurea, and chromatographed on 150 g of silica gel. Elution with 20–100% ethyl acetate in Skellysolve B gave major peaks corresponding to epimeric glycols of structure **4** (R = CH_2CCl_3). The less polar, 700 mg, showed one spot on tlc—silica gel, 50% ethyl acetate–cyclohexane; the more polar, 800 mg, showed two very close spots on the same tlc system. The R_f values of these trichloroethyl esters were similar but slightly greater than those of the corresponding methyl esters, above.

To 667 mg of the less polar glycol **4** (R = CH_2CCl_3) above was added 16.5 ml of pyridine and then, at 0°, 1.67 ml of methanesulfonyl chloride. The mixture was stirred at 0° for 10 min, and 1.75 hr longer with the ice bath removed. It was then again cooled to 0°, 15 ml of water was added, and the mixture was extracted with ethyl acetate. This was washed several times with cold dilute hydrochloric acid and aqueous sodium bicarbonate, dried, and evaporated. The crude bismesylate was stirred in 53 ml of acetone and 26 ml of water under nitrogen at 25° overnight. The solution was concentrated *in vacuo* and extracted with ethyl acetate, which was washed, dried, and evaporated. The residue was chromatographed on 75 g of silica gel and eluted with increasing amounts of ethyl acetate in Skellysolve B. After two main peaks of material, 276 and 103 mg, of unrearranged glycol monomesylates was eluted 34 mg of *dl*-8-isoprostaglandin E_1 trichloroethyl ester showing two olefinic protons between δ 5.0 and 6.0 (H_{13} at δ 5.28, J = 15 and 9.5 cps, and H_{14} at δ 5.7, J = 15 and 7 cps), two protons of the trichloroethyl group as a singlet, δ 4.8, and two carbinolic protons as multiplets between δ 3.9 and 4.5. This was followed by 12 mg of the trichloroethyl ester of *dl*-prostaglandin E_1, the nmr spectrum of which was identical with that obtained above.

The 34 mg of *dl*-8-isoprostaglandin E_1 trichloroethyl ester was dissolved in 1 ml of 90% acetic acid and stirred with 100 mg of zinc dust for 2 hr. It was then diluted with ethyl acetate which was washed several times with water, dried, and evaporated. The residue was chromatographed on 5 g of Silicar CC4 (Mallinckrodt) acid-washed silica gel and eluted with 50–100% ethyl acetate–Skellysolve B. The fractions corresponding in tlc mobility to 8-isoprostaglandin E_1[6] on the A IX system,[18] 15 mg, were combined and crystallized from ethyl acetate–Skellysolve B, mp 101–102°. This material showed no optical rotation between 475 and 230 nm, and the nmr and mass spectra were identical with those of the "natural" isomer.[6]

Anal. Calcd for $C_{20}H_{34}O_5$: C, 67.76; H, 9.67. Found: C, 67.56; H, 9.60.

***dl*-Prostaglandin A_1 and *dl*-Prostaglandin B_1 Methyl Esters.** A mixture (150 mg) of the less polar *erythro*- and *threo*-glycols (**3**) (R = CH_3) was treated in 4 ml of pyridine with 0.4 ml of methanesulfonyl chloride at 0° and then allowed to warm to room temperature over 2 hr. Ice was then added; the product was extracted with ethyl acetate and was washed with cold dilute hydrochloric acid, sodium bicarbonate, dried, and evaporated. The crude bismesylate was dissolved in 15 ml of acetone to which was added 2 ml of water and 4 ml of saturated sodium bicarbonate solution, and the resulting mixture was refluxed under nitrogen for 4 hr. After acidification, the mixture was extracted with ethyl acetate, and the extracts were washed, dried, and evaporated. The crude residue was briefly treated with excess ethereal diazomethane and chromatographed on 20 g of silica gel. Elution with increasing proportions of ethyl acetate in cyclohexane gave a total of 71 mg (50% yield) of a mixture of *dl*-PGA_1 and *dl*-PGB_1 methyl esters. These were not well separated by the column, but the early fractions of the main peak, 14 mg, consisted of pure *dl*-PGA_1 methyl ester, λ_{max}^{EtOH} 221 nm (ε 11,000), and identical mobility on several tlc systems[18] to natural material. The remainder of the material of the main peak, 56 mg (λ_{max} 219 (ε 7530), 278 nm (10,150), was a mixture consisting of 65% *dl*-PGA_1 methyl ester and 35% *dl*-PGB_1 methyl ester.

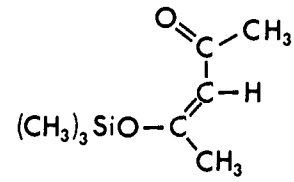
Acknowledgment. We wish to thank Dr. W. A. Struck and associates for analytical and some spectral data, and Dr. M. F. Grostic for mass spectra. We also acknowledge technical assistance by J. M. Baldwin, J. H. Kinner, and R. A. Morge.

Communications to the Editor

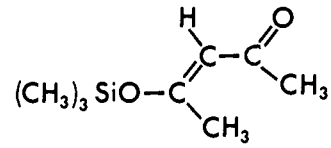
A Novel Stereochemical Rearrangement Process for an Isomer of Trimethylsilicon Acetylacetonate, a Silyl Enol Ether

Sir:

Nearly every element possessing metallic character is known to form compounds with acetylacetonate and other β-diketonates. In the majority of compounds, the metal is bonded to both donor oxygen atoms on the ligand, resulting in a cyclic chelate structure. In certain mercury(II)[1,2] and silicon(IV)[3,4] β-diketonates, however, the central atom is bonded to only one donor oxygen atom. Thus these compounds possess an open-chain enol ether structure in which the uncoordinated or "dangling" oxygen is ketonic. Such a structure has been assigned for trimethylsilicon acetylacetonate, $(CH_3)_3Si(acac)$.[3,4] In addition, the occurrence of isomers I and II has been claimed based on the coincidence of infrared absorption bands for the compound and the carbonyl stretching frequencies for the *cis* and *trans* isomers of the methyl enol ether of acetylacetone.[3] This communication reports some nmr studies of $(CH_3)_3Si(acac)$ which confirm the existence of the expected isomers and, more important, which show that one of the isomers undergoes a novel stereochemical rearrangement process.



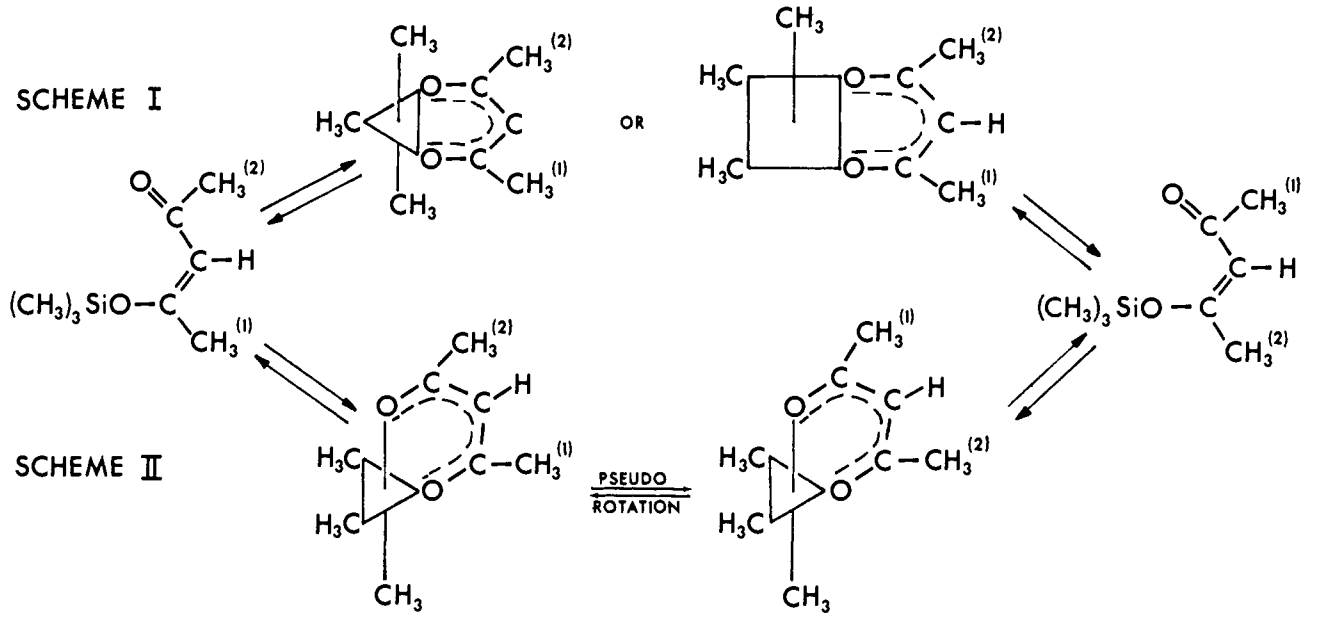
I



II

$(CH_3)_3Si(acac)$ was prepared and purified according to the method described by West.[4] *Anal.* Calcd for $C_8H_{16}O_2Si$: C, 55.77; H, 9.36; Si, 16.30; mol wt, 172. Found: C, 55.70; H, 9.21; Si, 16.51; mol wt ($C_6H_5NO_2$), 184. Vibrational frequencies $\nu_{C=O}$, $\nu_{C=C}$, and ν_{Si-O} were in agreement with the reported values and verify the previously assigned enol ether structure.[3,4]

(1) D. C. Nonhebel, *J. Chem. Soc.*, 738 (1963).
(2) G. S. Hammond, D. C. Nonhebel, and C. S. Wu, *Inorg. Chem.*, 2, 73 (1963).
(3) W. H. Knoth, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1954; *cf.*, L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 14.
(4) R. West, *J. Amer. Chem. Soc.*, **80**, 3246 (1958).



The lines observed in the proton magnetic resonance spectrum of the compound at room temperature are shown in Figure 1. The acetylacetonate moiety gives rise to a –CH= proton multiplet at τ 4.40, a –CH= singlet at τ 4.75, two methyl doublets at τ 7.70 and 8.01,

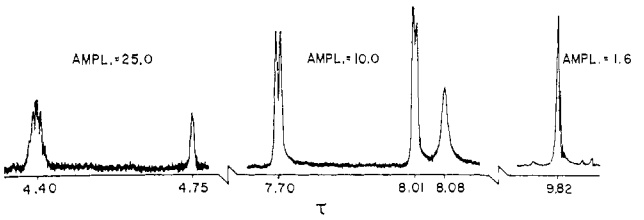


Figure 1. Proton nmr spectrum of $(CH_3)_3Si(acac)$ in chlorobenzene solution at 38.5° (60 MHz); concentration 11.4 g/100 ml of solvent.

and a methyl singlet at τ 8.08. Two partially resolved Si–CH_3 lines are present near τ 9.82. As the temperature is decreased, the methyl line at τ 8.08 broadens markedly and then splits into two rather sharp lines (see Figure 2). At −53.7°, the two Si–CH_3 lines are completely resolved, and the two –CH= lines remain essentially as observed at room temperature. The presence of two –CH= and two Si–CH_3 lines indicates that the $(CH_3)_3Si(acac)$ molecule occurs in two geometric forms. Furthermore, the line broadening phenomenon shows that one of the isomers undergoes a rapid configurational rearrangement process which averages two nonequivalent acetylacetonate methyl group environments.

The lines at τ 4.40, 7.70, and 8.01 in the room-temperature spectrum have relative integral intensities 1:3:3 and, along with the more intense Si–CH_3 line, are assigned to the *trans* isomer II. Unequivocal chemical shift assignments for the acetyl and allylic methyl protons on the acetylacetonate moiety must await investigation of other trialkylsilicon derivatives. A double-resonance experiment, however, has shown that the two types of methyl protons are both coupled to the vinylic proton. The temperature dependence of the coupling constants, 0.6 and 0.4 Hz at 38.6° *vs.* 0.45 and <0.3 Hz at −53.7°, respectively, is probably due to shifts in the equilibrium distribution of methyl group rotamers.

The line at τ 4.75 and the time-averaged methyl line at τ 8.08 of the labile isomer have relative integral intensities 1:6. These lines and the less intense Si–CH_3 line are assigned to the *cis* isomer I. In the absence of

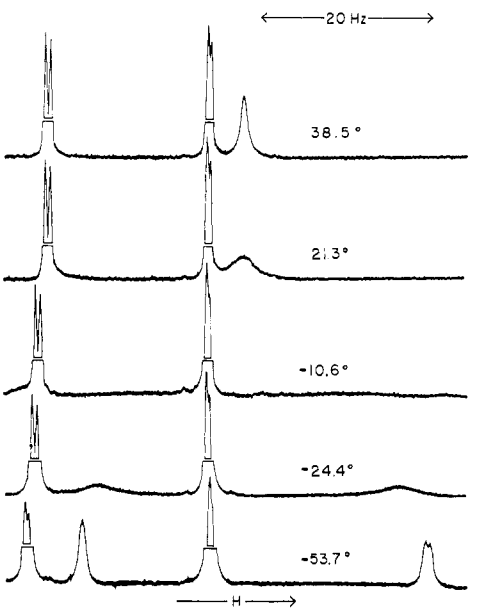


Figure 2. Temperature dependence of the acetylacetonate methyl proton resonance lines of $(CH_3)_3Si(acac)$; concentration 11.4 g/100 ml of chlorobenzene.

rapid acetylacetonate methyl group exchange at −53.7°, some coupling (~0.5 Hz) is observed between the vinylic proton and the acetylacetonate methyl group which appears at higher field (*cf.* Figure 2). It is noteworthy that a ground-state stereochemistry based on a trigonal bipyramid in which acetylacetonate acts as a bidentate ligand and spans an axial–equatorial edge cannot be assigned in place of the *cis* isomer. A trigonal-bipyramidal structure of this type should give rise to two Si–CH_3 lines in the absence of exchange. However,

only one, sharp Si–CH_3 resonance line is observed for the labile isomer at −53.7°, which is the result predicted for the *cis* enol ether structure. The ability of the *cis* isomer to undergo a rapid rearrangement which leads to environmental averaging of nonequivalent acetylacetonate methyl groups is attributed to the facile formation of a five-coordinated silicon intermediate, as shown in Schemes I and II. A similar process for the *trans* isomer should be hindered by rotation about the C=C bond. Indeed, no broadening of the acetylacetonate methyl lines for the *trans* isomer was observed even at 120°.

Mean lifetimes for the methyl protons in the two, equally populated, nonequivalent sites of the *cis* isomer were estimated at five temperatures in the range 20–40° from the fast-exchange approximation of Piette and Anderson.[5] No change in mean lifetimes was observed on doubling the solute concentration in chlorobenzene. Also, a solution containing $(CH_3)_3Si(acac)$ and free acetylacetone in relative amounts 3:1 showed no broadening of the free ligand methyl line under conditions where rearrangement of the *cis* isomer is fast. These results, which indicate that the rearrangement is first order and that an intramolecular mechanism operates, are in agreement with the processes shown in Schemes I and II. Values of first-order rate constants for the five temperatures investigated gave an estimated Arrhenius activation energy of 15 ± 4 kcal/mole and a frequency factor of exp(14.3 ± 3.0). A more detailed nmr line-shape analysis of the rearrangement kinetics is in progress.

Acknowledgment. We wish to acknowledge support of this research by the National Science Foundation, Grant GP-9503.

(5) L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959), eq 23.

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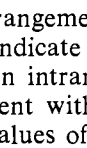
Anodic Alkyl Transfer from Hydroquinone Ethers. II.[1] Anodic Oxidation of an α-Tocopherol Model Compound

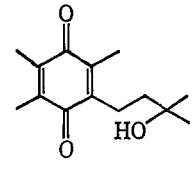
Sir:

We report the first case of a reversible two-electron oxidation of a phenol in aprotic media. The α-tocopherol model compound (I) undergoes quasi-reversible oxidation at a platinum electrode in acetonitrile. A 1.0 m*M* solution of I in acetonitrile exhibits an oxidation peak at +0.76 V[2] at a stationary platinum electrode. The peak current at a voltage sweep rate of 10 V/min is 170 μA. Two well-characterized one-electron oxidation systems, 9,10-diphenylanthracene[3a] and 4,4′-dimethoxystilbine,[3b] give peak currents of 90 and 93 μA, respectively, under the same conditions. Therefore, the oxidation of I involves the transfer of two electrons.[4] When the direction of the potential scan is switched in the cathodic direction after the initial anodic peak, a reduction peak is observed at +0.60 V. The ratio of cathodic to anodic peak currents, i_{pc}/i_{pa}, was determined to be equal to 0.78, indicating that the dication is fairly stable during the time scale of cyclic voltammetry.



I

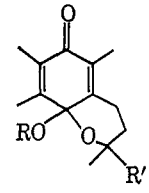
Controlled potential coulometry of I in either acetonitrile or acetonitrile–acetic acid (3:1) containing sodium acetate (0.25 *M*) resulted in the consumption of 2 Faradays per mole of substrate. A preparative electrolysis in the latter media resulted in the formation of the quinone II. The structure of II was established



II

on the basis of ir, nmr, and mass spectra as well as from a voltammetric study.

Chemical oxidation of I with alkaline ferricyanide or benzoquinone results in the formation of a spiro dimer thought to form *via* the quinone methide.[5] α-Tocopherol oxidation in ethanol[6] or dry acetonitrile containing acetate ion[7] results in the formation of the corresponding dienone III. The latter observations have been cited as evidence that the cyclic hemiacetal IIIc is



IIIa, R = Et
b, R = Ac
c, R = H

an intermediate in the chemical oxidation of α-tocopherol to α-tocopherylquinone. The direct formation of II, rather than IIIb, when the oxidation is carried out in the presence of high acetate concentration is indicative that the anodic generation of the quinone does not involve hemiacetal formation. However, it has been observed that the oxidation of α-tocopherol in the presence of a small amount of water in aprotic media containing a large excess of acetate ion results only in the formation of IIIc.[7] Further study is necessary to clarify this point.

The quinone II is reduced at −0.56 V (R_1) in acetonitrile containing lithium perchlorate. When the potential sweep is reversed after R_1, a corresponding oxida-

(1) Part I: V. D. Parker, *Chem. Commun.*, 610 (1969).
(2) All potentials refer to the aqueous saturated calomel electrode.
(3) (a) M. E. Peover and B. S. White, *J. Electroanal. Chem.*, **13**, 93 (1967); (b) V. D. Parker and L. Eberson, *Chem. Commun.*, 340 (1969).
(4) While the over-all result of the oxidation is the transfer of two electrons, the detailed mechanism may involve two closely spaced one-electron steps.
(5) J. L. G. Nilsson, *Acta Pharm. Suecica*, **5**, 1 (1969).
(6) P. D. Boyer, *J. Amer. Chem. Soc.*, **73**, 733 (1951).
(7) W. Durckheimer and L. A. Cohen, *ibid.*, **86**, 4388 (1964).