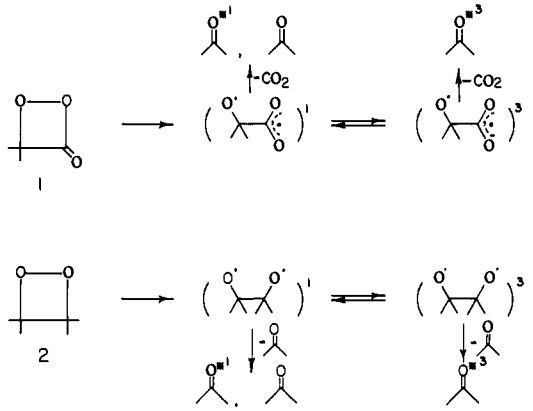
Table I. Dioxetanone Structures and Relative Energies

R_{O-O}, Å	R_{C-C}, Å	∠COO[a]	∠COO[b]	E, au	ΔE, kcal/mol	highest occupied orbital 4a'', au	virtual 16a', au[c]	anion energy ΔE, kcal/mol
1.503	1.502	89.5	90.5	−300.8921	0.0	−0.483	0.138	0.0
1.525	1.502	89.0	90.0	−300.8919	0.2	−0.486	0.127	−8.5
1.55	1.502	88.5	89.5	−300.8910	0.7	−0.489	0.114	−17.0
1.60	1.501	87.7	88.4	−300.8877	2.8	−0.493	0.090	−31.2
1.70	1.501	85.5	86.5	−300.8765	9.8	−0.501	0.046	−51.9

[a] The methylene carbon atom is referred to. [b] The carbonyl carbon atom is referred to. [c] The 16a' orbital is not the lowest virtual at the equilibrium geometry. This orbital crosses the 5a'' between R_{O-O} equals 1.525 and 1.55 Å.

Scheme I



peroxide is lifted ca. 21° from the plane defined by the remaining ring atoms.

Of significance to the understanding of the thermal chemistry of dioxetanone is the prediction that stretching the oxygen–oxygen bond does not cause a concomitant increase in the length of the ring carbon–carbon bond (Table I). Although we have not carried the calculations all the way through to the transition state, progress along the reaction coordinate is significant since the energy increase obtained is a substantial fraction of the experimentally determined activation enthalpy for dioxetanone **1**.[13] The implication of these findings is that the thermolysis of dioxetanone may proceed through the biradical state formed by crossing of the 14a′ and 16a′ orbitals as a result of cleavage of the oxygen–oxygen bond. A similar conclusion was reached by Goddard and Harding[14] for dioxetane by using GVB calculations. This conclusion is supported by extensive experimental evidence.[15]

These findings suggest an explanation for the difference in excited-state yields obtained from thermolysis of dioxetanone **1** and dioxetane **2**. Cleavage of the oxygen–oxygen bond in both cases leads to a biradical presumably initially in a singlet state. Intersystem crossing to the triplet biradical is therefore in competition with cleavage of the ring carbon–carbon bond (Scheme I). For the case of dioxetanone the loss of CO_2 competes with intersystem crossing; for dioxetane it is the loss of a simple carbonyl compound that is in competition with intersystem crossing. The former is more exothermic and, therefore, is probably more rapid, giving the biradical less opportunity to cross to the triplet manifold. Consistent with this postulate is the experimental observation that the yield of excited singlet acetone from thermolysis of **1** and **2** is quite similar, but the yield of triplet acetone from **1** is considerably reduced from that of **2**.[3]

Our formulation of the CIEEL mechanism has as a key tenet the activated transfer of an electron from an electron donor to the peroxide.[16] We postulate further that the oxygen–oxygen bond of the peroxide cleaves either simultaneously with the transfer of the electron or very rapidly following its arrival. Several of the results of the calculation bear on this mechanism. First, transfer of an electron from an activator (perylene, for example) to dimethyldioxetanone is estimated from electrochemical data to be endothermic at the equilibrium ground-state geometry.[19] Indeed, we have measured the activation energy for this process and find it to be 16 kcal/mol. The calculations show that stretching the oxygen–oxygen bond of dioxetanone results in a large decrease in the energy of the unoccupied 16a′ orbital (Table I), thereby facilitating the electron transfer. Thus, as we have previously suggested, the activating process for the electron transfer in the CIEEL mechanism is most likely stretching of the oxygen–oxygen bond.

The second result of the calculation that aids in the description of the CIEEL mechanism concerns the energy of the radical anion obtained by placing an electron in the 16a′ orbital. This orbital is antibonding between the peroxide oxygens (Figure 2d). Table I contains the change in energy of the anion as a function of oxygen–oxygen bond distances. The striking result is that on increasing this bond distance 0.2 Å from its equilibrium value, the energy of the anion drops by ca. 52 kcal/mol. We take this result to indicate that the oxygen–oxygen bond of the radical anion of dioxetanone is dissociative and irreversible cleavage follows immediately the receipt of the electron. This conclusion is entirely consistent with our experimental observations on the dioxetanone system.

In sum, these calculations provide new insight into the detailed chemistry of dioxetanone, though highly quantitative predictions will require more extensive calculations. They substantiate a reasonable rationalization of the different yields observed from dioxetanone **1** and dioxetane **2** and provide some confirmation of the major postulates of the CIEEL mechanism.

Acknowledgment. We thank Peter Dardi and Suketu Gandhi for assistance in generating the MO plots. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Office of Naval Research and the National Science Foundation.

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C-20 Stereospecific Introduction of a Steroid Side Chain

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The development of sterochemically controlled syntheses of steroid side chains in recent years has been spurred by the bio-

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logical significance of new natural products containing modified cholesterol side chains.[1] We have been particularly interested in practical new routes to the therapeutically important vitamin D_3 metabolites, 25-hydroxycholecalciferol and 1,25-dihydroxycholecalciferol.[2] The focal point of any such synthesis is the stereospecific introduction of the asymmetric center at C-20.

The potential large-scale availability of 17-keto steroids, particularly dehydroepiandrosterone (**1b**), makes them attractive as starting materials. Here we report on a new and efficient method for the stereospecific introduction of a five-carbon side chain which is suitably functionalized for further elaboration.

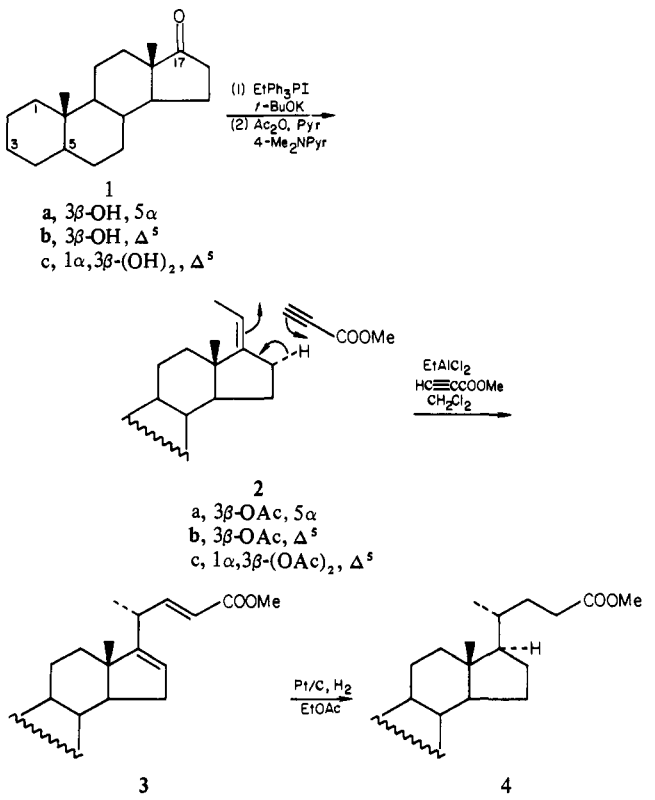
When this work was initiated, the only stereospecific steroid side chain synthesis involved the use of organopalladium chemistry.[3] There then appeared a route which took advantage of a stereoselective alkylation of an initially introduced acetic acid ester side chain and subsequent conversion of the carboxylate function to the C-21 methyl group.[4] More recently, elaboration of pregnenolone derivatives by Carroll[5] and oxy-Cope[6] rearrangements have been reported.

Our process utilizes as the key step an ene reaction of an appropriately substituted (*Z*)-17-ethylidene steroid to stereospecifically generate the chiral center at C-20. The stereochemical control is attributed to the virtually exclusive attack of the enophile at the less hindered α face of the olefin.

Initial attempts to carry out an ene reaction with methyl propiolate and (*Z*)-3β-acetoxy-5α-pregn-17(20)-ene (**2a**)[7] under the usual thermal[8] or Lewis acid catalyzed[9] conditions were unsuccessful. Use of the standard Lewis acids led to decomposition of **2a** via a Wagner–Meerwein rearrangement[10] of the C-17 cation formed from protonation of the double bond. This problem has been overcome by the use of ethylaluminum dichloride, which, in addition to functioning as Lewis acid, acts as a proton scavenger.[11] Thus, addition of pure (*Z*)-3β-acetoxy-5α-pregn-17-(20)-ene (**2a**) to a solution of 1.4 equiv of methyl propiolate and 2.3 equiv of ethylaluminum dichloride (a stoichiometric amount of Lewis acid is required, as well as an additional equivalent for every Me). site in the ene component[11]) in methylene chloride produced, after 2 h at room temperature, an 89% yield (stereochemically pure by GC) of the ene product **3a**,[12] mp 105–106 °C; $[\alpha]_D$ +30.0°; NMR 6.92 (dd, J = 8, 16 Hz, 1 H, C-22 H), 5.78 (dd, J = 1.5, 16 Hz, 1 H, C-23 H), 5.39 (m, 1 H, C-16 H), 3.69 (s, 3 H, OMe), 2.98 (qd, J = 7,8 Hz, 1 H, C-20 H), 1.16 (d, J = 7 Hz, 3 H, C-21 Me), 0.83 (s, 3 H, C-19 Me), and 0.74 ppm (s, 3 H, C-18 Me).

It was gratifying to learn that under the same conditions, the $\Delta^{5,17(20)}$-diene **2b**,[7] reacted exclusively on the side chain to give the $\Delta^{5,16}$-ester **3b** (86% yield, stereochemically pure by GC), mp 124–125 °C; $[\alpha]_D$ −24.8°; NMR 6.92 (dd, J = 8, 16 Hz, 1 H, C-22 H), 5.80 (dd, J = 1.5, 16 Hz, 1 H, C-23 H), 5.40 (m, 2 H, C-6 H and C-16 H), 3.69 (s, 3 H, OMe), 3.00 (qd, J = 7,8 Hz, 1 H, C-20 H), 1.17 (d, J = 7 Hz, 3 H, C-21 Me), 1.03 (s, 3 H, C-19 Me), and 0.78 ppm (s, 3 H, C-18 Me). This intermediate

Scheme I



1
a, 3β-OH, 5α
b, 3β-OH, Δ^5
c, 1α,3β-$(OH)_2$, Δ^5

2
a, 3β-OAc, 5α
b, 3β-OAc, Δ^5
c, 1α,3β-$(OAc)_2$, Δ^5

3 4

should be useful for further elaboration to 25-hydroxycholesterol.

Our primary target, however, was the synthesis of 1,25-dihydroxycholesterol. Of crucial importance to the efficiency of this process was the availability of 1α-hydroxydehydroepiandrosterone (**1c**)[13] from the microbial hydroxylation[14] of dehydroepiandrosterone (**1b**).

Thus, the dihydroxy ketone **1c** was converted by a Wittig reaction (2 mol of $EtPh_3PI$, 2 mol of *t*-BuOK, THF, room temperature, 16 h, then reflux 2 h) followed by acetylation in situ (excess Ac_2O, pyridine, 1.5% 4-(dimethylamino)pyridine) to the (*Z*)-17-ethylidene diacetate (**2c**), mp 90–91 °C; $[\alpha]_D$ −24.1°; NMR 5.11 (M, 2 H, C-20 H and C-1 H), 5.53 (m, 1 H, C-6 H), 1.63 (d, J = 7 Hz, 3 H, C-21 Me), 1.09 (s, 3 H, C-19 Me), and 0.88 ppm (s, 3 H, C-18 Me).

The ene reaction of a 94:6 *Z*/*E* mixture of **2c**[15] (89% on **1c**) (1.5 equiv of methyl propiolate and 3.1 equiv of ethylaluminum dichloride, CH_2Cl_2, 1.75 h, room temperature) gave, after chromatography, the pure 20(*R*)-ester **3c**[16] (89% yield) as an amorphous solid, $[\alpha]_D$ + 5.5°; NMR 6.90 (dd, J = 8, 16 Hz, 1 H, C-22 H), 5.77 (dd, J = 1, 16 Hz, 1 H, C-23 H), 5.51 (m, 1 H, C-6 H), 5.38 (br s, 1 H, C-16 H), 2.98 (qd, J = 7,8 Hz, 1 H, C-20 H), 1.14 (d, J = 7 Hz, 3 H, C-21 Me), 1.08 (s, 3 H, C-19 Me), and 0.75 ppm (s, 3 H, C-18 Me).

The catalytic reduction of the C-16 double bond delivers hydrogen exclusively from the less hindered α face.[17] Reduction

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(16) By running the reactions to 90–92% completion, the contaminating *E* isomer remained substantially unreacted and only 2–3% of the unnatural C-20 *S* isomer was produced. This small amount can be removed by chromatography or crystallization at a later stage.

of C-16 and C-22 double bonds can readily be accomplished under conditions which leave the C-5 double bond untouched.[18] Thus hydrogenation at atmospheric pressure (5% Pt/C, EtOH, or EtOAc) ceased cleanly with the absorption of 2 equiv to give the Δ^5-ester **4c** (78% yield on **3c**)[19], mp 110.5–112 °C; $[\alpha]_D$ −19.0°, NMR 5.52 (m, 1 H, C-6 H), 3.62 (s, 3 H, OMe), 1.06 (s, 3 H, C-19 Me), 0.90 (d, J = 6 Hz, 3 H, C-21 Me), and 0.65 ppm (s, 3 H, C-18 Me).

Note Added in Proof: Since this paper was submitted a similar report using our methodology for the Lewis acid catalyzed ene reaction has appeared.[20]

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Laser-Desorption Mass Spectrometry/Mass Spectrometry and the Mechanism of Desorption Ionization

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Two newer aspects of mass spectrometry, desorption ionization and mass spectrometry/mass spectrometry, are subjects of increasing interest for their utility and the chemistry they access. The desorption methods, including field desorption,[1] plasma desorption (fission fragment mass spectrometry),[2] secondary ion mass spectrometry,[3] electrohydrodynamic ionization,[4] and laser desorption[5] have had remarkable success in extending the coverage of mass spectrometry to involatile and thermally labile compounds. Mass spectrometry/mass spectrometry has allowed characteristic spectra to be taken for individual constituents in complex mixtures[6] and is also contributing to our knowledge of ion structures and chemistry.

We now report, for the first time, spectra obtained by combining laser desorption with mass spectrometry/mass spectrometry. Remarkable similarities in fragmentation behavior with secondary ion mass spectra (SIMS) are evident, and this provides evidence for mechanistic similarities[7] between SIMS and laser desorption (LD). Attachment of alkali metals to organic molecules (cationization) is a common feature of desorption ionization while numerous other metals, including Ag, Cu, Pt, Al, Fe, etc., have long been known to cationize organic molecules under conditions of ion bombardment.[8] We now show that this process also occurs during laser desorption of involatile compounds which further indicates the existence of underlying similarities between LD and SIMS.[9] The procedures used here are also noteworthy, because steady ion currents (several thousand ions per laser pulse) of cationized sucrose are obtained for relatively long periods (minutes).

Figure 1 shows the LD mass spectrum of sucrose supported on silver foil in the presence of ammonium chloride.[10] Similar spectra, excluding the NH_3-adduct ions, were obtained without ammonium chloride which was added to the sample because of its demonstrated effect in enhancing ionization in SIMS.[12] The laser-desorption spectrum shows cation (Ag^+) attachment to sucrose to yield m/z 451/449 as the dominant high-mass species.[13] The products of glycosidic cleavage with retention of the metal ion (m/z 289/287) and of this cleavage followed by dehydration (m/z 271/269) represent the most abundant fragment ions, although some dehydration of the cationized molecule is also observed. All four ions $(Ag + S)^+$, $(Ag + S–H_2O)^+$, $(Ag + G)^+$, and $(Ag + G–H_2O)^+$ (S = sucrose, G = glucose) occur in similar relative abundances in the SIMS spectrum (Figure 2) of sucrose supported on silver.[12] Differences of note between the spectra are the ammonia-solvated ions [including $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$ seen at lower mass] which occur in the LD spectrum and the inorganic cluster ions (Ag_3^+, Ag_3Cl^+, $Ag_3Cl_2^+$) and the sodium cationized molecule which are observed in SIMS. A preliminary interpretation is that laser desorption at these power densities causes thermal generation of NH_3. It is also apparent that the internal energy of the cationized molecule, $(Ag + S)^+$ is largely independent of the method of ionization.[14]

Figure 3 shows the mass-analyzed ion kinetic energy (MIKE) spectrum or MS/MS spectrum (MS/MS = mass spectrometry/mass spectrometry) for one of the isotopic forms of silver

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(9) It is noteworthy that ICR experiments show the attachment of metal ions (including Ag^+) to gas-phase organic molecules on laser irradiation of the metal, see: Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641.
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(14) Compare also: Busch, K. L.; Unger, S. E.; Cooks, R. G. In "Proceedings of Ion Formation From Organic Solids Workshop"; Benninghoven, A., Ed.; Unveristy of Münster: Münster, Germany; to be published by Springer-Verlag.

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