Table II. ESR Parameters and (K^+_{free}) for Added Concentrations of $KClO_3$ Added to the Anion Radical of 2,6-Di-*tert*-butylbenzoquinone in HMPA

$(KClO_3)_{total}$[a]	$1/(A^\circ - \bar{A})$, G^{-1}	(K^+_{free})	$(K^+)_{metal}$[b]	K_a
0.05085	12.209	0.02927	0.00059	26.7
0.05328	12.043	0.02983	0.00098	29.4
0.05252	11.938	0.03019	0.00095	27.2

[a] All concentrations are given in *M*. [b] $(K^+)_{metal}$ is the contribution to the total concentration of potassium due to the potassium metal used to reduce the quinone.

mined. The concentration of the potassium ion free of ion pairing (K^+_{free}) can be calculated from this coupling constant. Since the difference between the total added salt concentration and (K^+_{free}) is the concentration of the diamagnetic ion pair, K_a for this new salt can be calculated. The anion radical concentration (about 10^{-5} *M*) is small compared to the concentration of added salt, so there is no need to account for the reduction in (K^+_{free}) due to ion pairing with the anion radical.

The addition of 0.0493 *M* KI to the anion radical solution of 2,6-di-*tert*-butylbenzoquinone in HMPA results in an observed coupling constant of 2.246 G. By the use of eq 3, (K^+_{free}) is found to be 0.0422 *M*. This corresponds to a value for K_a of 4.0. The very small value for K_a of KI necessarily leads to a large error in K_a, since (K^+, I^-) must be determined from a small difference between two large numbers. From 12 independent measurements, each from a different sample of anion radical, K_a for KI was found to 4.3 ± 1.9. This standard deviation, while large, is small in comparison with conductivity measurements. Salts with very low K_a's cannot even be determined by conductivity.

Potassium chlorate was studied in the same manner. Table II shows a representative set of data leading to a value for K_a of 27.7 ± 2.5.

Brusset and coworkers[8] have concluded from their curve of conductivity vs. concentration that KI is not fully dissociated in HMPA. However, they were not able to obtain K_a. The work presented here describes a new method for the determination of ion association constants and the only method that can be used effectively in highly solvating media such as HMPA.

It should be mentioned that the technique described here has been applied to the potassium ion only, due to the fact that conductivity data are scarce for other cations. However, there is no reason why, with future measurements, this technique could not be expanded to include other cations and other solvent systems. For systems with very small K_a's, large errors are generated due to the fact that the ion pair concentration is found from a small difference between two large numbers. For systems with very large K_a's, high concentrations of the salt must be added to the solution to generate enough free cation to interact with the 2,6-di-*tert*-butylsemiquinone. Concentrations higher than about 0.4 *M* are undesirable due to their effect upon the bulk properties of the solvent. For these reasons the technique described here is limited to the study of salts with K_a's more or less between 3 and 200. Finally it should be mentioned that the concentrations of free ions are necessarily small, and rough calculations indicate that ionic strength changes are not a significant factor. A more detailed analysis of the effects of activity coefficients and saturation factors will appear in a future publication.

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A Synthesis of Optically Active Avenaciolide from D-Glucose. The Correct Stereochemistry of the Natural Product

Sir:

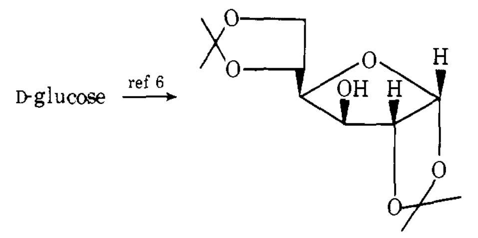
Carbohydrates and their derivatives possess several attributes which make them ideal precursors for certain target molecules in synthetic organic chemistry. Four of the more obvious attributes are (i) enantiomeric purity, (ii) the high conformational bias usually displayed which results in reactions having a high degree of stereoselectivity, (iii) the ready assignment of stereochemistry by means of NMR methods which have been honed to a remarkable degree of sophistication for the analysis of carbohydrate derivatives,[1] and (iv) the intensive assembly of functional groups which can be selectively utilized through employment of appropriate protecting groups.

A consequence of attributes (i) and (ii) is the possibility to incorporate the absolute configuration of the target molecule into the synthetic planning. This general approach is particularly advantageous in the synthesis of chiral, biologically active substances, since usually only one enantiomer is effective owing to the enantioselectivity of chemoreceptors in nature.[2] Furthermore with many of these substances, the absolute stereochemistry cannot be determined directly, and derivatization or chemical transformation to known chiral products is fraught with danger. As a case in point, and in exemplification of the above-described attributes, we outline herein a synthesis[3] of optically active avenaciolide[4] (**1**) from D-glucose by a route which establishes the correct chirality of the naturally occuring enantiomer.[5]

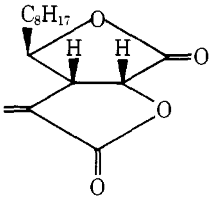
Relationships immediately apparent between "diacetone glucose" (**2**)[6] and avenaciolide (**1**) are (a) the presence in **2** of two of the three asymmetric centers in **1** at the proper oxidation level, (b) the presence in **2** of one of the potential lactones of **1** in the guise of the protected anomeric center, (c) the free hydroxyl group as a site for elaboration of the acetic acid unit of **1**, and (d) the 5,6-acetonide which offers ready access to the *n*-octyl group.

Objectives (c) and (d) had in fact been already realized by Rosenthal and Nguyen[7] in the conversion of **2** to the aldehyde **3**.

The conversion of **3** to avenaciolide is outlined in Scheme I. In view of the ease with which 4-aldehydo ribofuranosides epimerize,[8] it was necessary to ensure that the compound obtained in the Wittig reaction of **3** ($C_7H_{15}P^+Ph_3Br^-$, THF, BuLi, room temperature, 70%) was indeed **4** (Anal. ($C_{18}H_{30}O_5$) C, H). Had such an epimerization occurred the

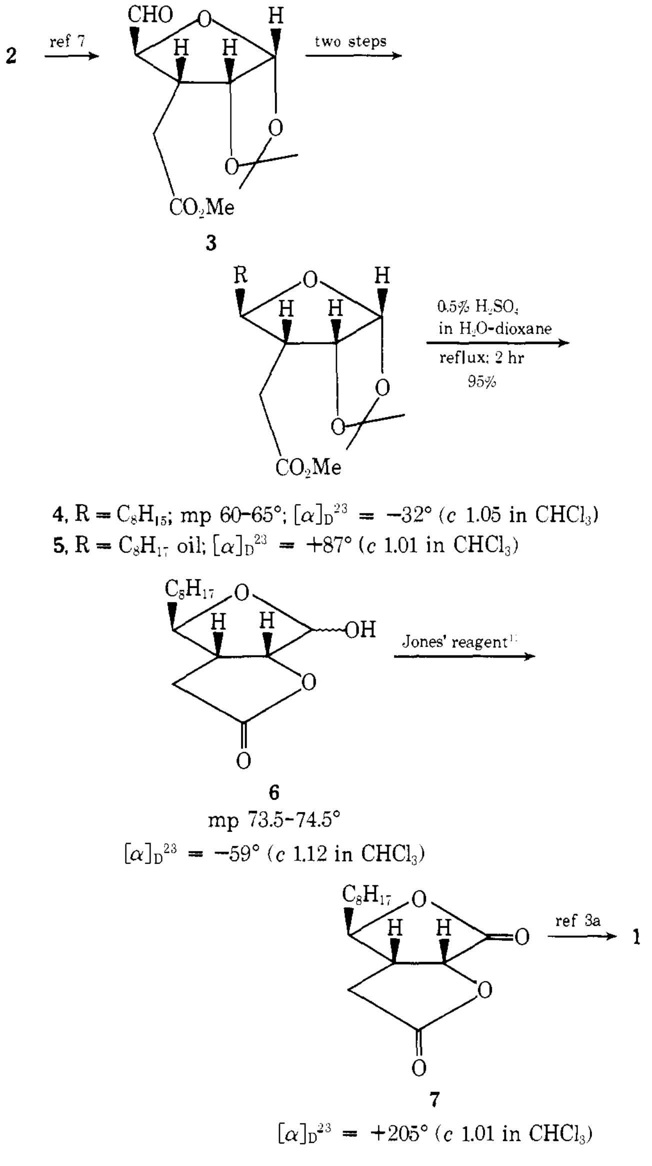


2
"diacetone glucose"



1

Scheme I



2 → **3**

4, R = C_8H_{15}; mp 60–65°; $[\alpha]_D^{23}$ = −32° (*c* 1.05 in $CHCl_3$)
5, R = C_8H_{17} oil; $[\alpha]_D^{23}$ = +87° (*c* 1.01 in $CHCl_3$)

6
mp 73.5–74.5°
$[\alpha]_D^{23}$ = −59° (*c* 1.12 in $CHCl_3$)

7
$[\alpha]_D^{23}$ = +205° (*c* 1.01 in $CHCl_3$)

sequence in Scheme I would have yielded isoavenaciolide, contrary to the experimental results.

Hydrogenation of **4** in ethanol over 10% Pd–C afforded **5** (87%) as a noncrystalline material (*m/e* 328 (M), 327 (M − 1). Treatment with acid caused simultaneous removal of the acetonide and lactonization to the hemiacetal **6** in 95% yield (Anal. ($C_{14}H_{24}O_4$) C, H). Oxidation[11] of **6** afforded the bislactone **7** (77%) which had been obtained previously in racemic form by Parker and Johnson, in the first synthesis of *dl* avenaciolide.[3a] Accordingly **7** was transformed to **1** in 50% yield as described by these workers.[3a] The resulting material had a ^{1}H NMR spectrum identical with a sample of the *dl* mixture kindly supplied by Dr. Johnson.[3a]

For this preparation of **1**, mp 50–51° and $[\alpha]^{29.5}$D = −41.08° (*c* 0.274 in EtOH).[9] (Anal. ($C_{15}H_{22}O_4$) C, H). For naturally occuring avenaciolide[4], mp 49–50°, 54–56° and $[\alpha]^{26.5}$D = −41.6° (*c* 1.27 in EtOH). For *dl*-avenaciolide,[3] mp 54–57°.

The foregoing therefore indicates that the chirality of naturally occuring avenaciolide is (3a*R*, 4*R*, 6a*R*) and not (3a*S*, 4*S*, 6a*S*) as previously suggested.[4,5] In addition configurational assignments of this entire series of fungicides are also probably incorrect, since these had been related to avenaciolide.[10] Syntheses of these analogs are underway and will be reported in due course.

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Molybdenum(0) and Tungsten(0) Interactions with Olefins. Direct Observation of Reversible Hydrogen Exchange Processes by Nuclear Magnetic Resonance

Sir:

Molybdenum and tungsten species are known to catalyze several olefin reactions (e.g., metathesis) but little mechanistic data are available. We present here some studies on the interaction of olefins with zerovalent complexes of these metals and the observation of hydrogen transfer processes central to several catalytic processes.