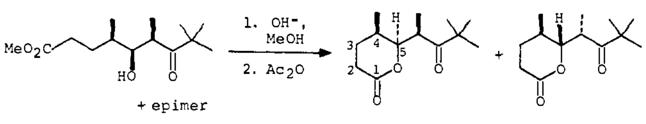
Table I

	4		**5**		
R	Yield, %[a]	$J_{2,3}$, Hz	Yield, %[d]	$J_{2,3}$, Hz	Mp, °C
Ph	86	5	77	4	Oil[b]
i-Pr	86	*c*	50	4	Oil
$PhCH_2$	90[d]	*c*	76	*c*	119-120

[a] Yields are crude and have not been optimized. [b] Lit.[10] mp 65-66 °C. Although this hydroxy acid has failed to crystallize in our hands, its stereostructure was determined by direct comparison with authentic **5a** and its threo diastereomer. [c] Splitting was complicated by other adjacent protons. [d] After hydrolysis of the trimethylsilyl group.

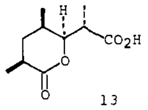
Table II

Aldehyde	Enolate	Ratio of **9**:**10**
6a	**8**	86:14
6b	**8**	74:26
6a	**7**	81:19



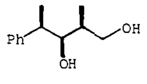
11 (74%) 12 (26%)

^1H NMR spectra shows that the signals for the C-5 protons appear as a triplet (J = 7 Hz) and a double doublet (J = 10 and 2 Hz) for the major and minor isomers, respectively. The analogous proton in the Prelog–Djerassi lactone (**13**) appears as a double doublet (J = 9.5 and 3.8 Hz).[13] Thus we assign the stereostructures for **11** and **12** as shown.



13

The hydroxy ketone mixture from the condensation of enolate **7** with aldehyde **6a** was cleaved by periodic acid in methanol and the mixture of β-hydroxy acids was esterified with diazomethane and separated by chromatography. The separated β-hydroxy esters were reduced using lithium aluminum hydride. The major hydroxy ester yielded diol **14** (mp 96.5-98 °C, lit.[11] mp 98-98.5 °C), and the minor hydroxy ester yielded diol **15** (mp 69-70.5 °C, lit.[11] mp 70.5-71 °C).



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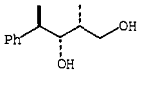
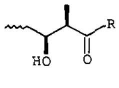
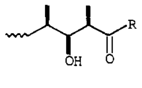


15

The results reported here provide the first steps toward our ultimate goal of constructing polyhydroxycarboxylic acids such as **1** by a series of stereoselective aldol condensations. At this point, we are able to introduce the three-carbon unit I with excellent selectivity and the four-carbon unit II in lower, but still acceptable, selectivity.



I



II

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Low-Temperature Nuclear Magnetic Resonance Evidence for Stereochemical Rigidity in Eight-Coordinate Metal β-Diketonates

Sir:

Until very recently,[1,2] NMR studies of eight-coordinate tetrakis chelates have failed to provide stereochemical and kinetic information because these chelates undergo very rapid stereochemical rearrangements. Previous low-temperature studies of tetrakis β-diketonates,[3,4] tropolonates,[5] and *N*,*N*-dialkyldithiocarbamates[6-8] have afforded only time-averaged NMR spectra. Only for the tetrakis(*N*,*N*-dimethyldithiocarbamato)tantalum(V) cation, $[Ta(S_2CNMe_2)_4]^+$,[1] and the heterochelate tris(5-methylpicolinato)(5,7-dichloro-8-quinolinolato)tungsten(IV), $W\overline{P}_3Q$,[2] have limiting slow-exchange spectra been reported. $[Ta(S_2CNMe_2)_4]^+$ exhibits two equally intense dithiocarbamate methyl resonances below the coalescence temperature of −62 °C,[1] consistent with the dodecahedral *mmmm*-D_{2d} stereoisomer found in the solid state.[9] $W\overline{P}_3Q$ displays two methyl resonances at room temperature.

Using the Freon solvent $CHClF_2$, we have investigated the ^1H NMR spectra of metal tetrakis(β-diketonates) at considerably lower temperatures than employed in earlier work,[3] and we have identified several zirconium(IV) and uranium(IV) β-diketonates which become stereochemically rigid on the NMR time scale at temperatures in the range of −100 to −170 °C. Typical spectra for tetrakis(acetylacetonato)zirconium(IV), $Zr(acac)_4$, are presented in Figure 1. The single, time-averaged methyl resonance characteristic of the higher temperatures splits into two lines of equal intensity below the coalescence temperature of −145 °C. The frequency separation in the slow-exchange limit is 11.1 Hz at 90 MHz (0.12 ppm), and the minimum line width below coalescence is ~6 Hz (at −163 °C); below −163 °C the line width increases owing to viscosity broadening. No splitting was observed for the ring proton resonance.

Low-temperature NMR spectra of $U(acac)_4$ (Figure 2) exhibit the same features found for $Zr(acac)_4$; however, the chemical shifts are appreciably larger and temperature dependent because of the paramagnetism of uranium(IV). The

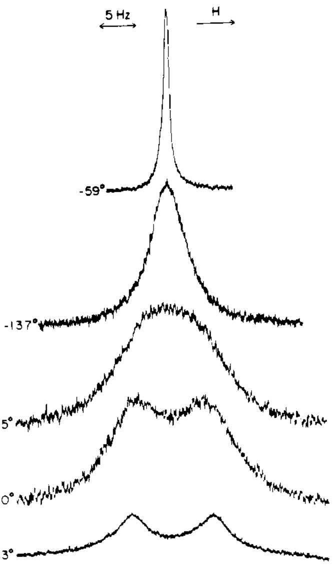

Figure 1. Methyl proton resonances for Zr(acac)$_4$ in CHClF$_2$ solution, 10 mg/mL, at 90 MHz.

methyl resonance broadens with decreasing temperature while the ring proton resonance remains relatively sharp. At −137 °C, the approximate coalescence temperature, the methyl resonance is so broad that it cannot be detected above the noise level. Below −137 °C, two methyl resonances of equal intensity emerge, and these become increasingly sharper until viscosity broadening sets in below −161 °C. The frequency separation between the two methyl resonances at −161 °C is 2403 Hz at 90 MHz (26.7 ppm).

The spectra in the slow-exchange limit are most simply interpreted in terms of the presence of a single stereoisomer which has two equally populated methyl environments and one ring proton environment. Of the nine possible square antiprismatic and dodecahedral stereoisomers,[10,11] five (*llll*-D_4, *llss*-C_2, *aabb*-D_2, *mmgg*-C_2, and *abmg*-C_1) may be ruled out on the basis of the number of the observed resonance lines. Consistent with two methyl resonances and a single ring proton resonance are the three dodecahedral stereoisomers *mmmm*-D_{2d}, *gggg*-D_2, and *gggg*-S_4, and the square antiprismatic stereoisomer *ssss*-D_2. In the solid state, Zr(acac)$_4$[12] adopts a structure which most closely approximates that of the idealized *ssss*-D_2 stereoisomer; however, the "square" faces of the antiprism are *slightly* folded about one diagonal, a distortion which, if carried far enough, converts the D_{4d} square antiprism to the D_{2d} dodecahedron.[12] U(acac)$_4$ is found in two crystalline modifications, an α form[13] and a β form.[14] β-U(acac)$_4$ is isomorphous with Zr(acac)$_4$, and the molecules in the β form have the same slightly distorted *ssss*-D_2 square antiprismatic structure.[14] The geometry of M(acac)$_4$ molecules in the α crystalline form has been described as predominantly square antiprismatic[15] and as predominantly dodecahedral,[16] but it has recently been shown[17] that the coordination group in α-M(acac)$_4$ most closely approximates a bicapped trigonal prism and the ligand wrapping pattern corresponds to the $h_1h_1p_2p_2$-C_2 stereoisomer described by Porai-Koshits and Aslanov.[18] The $h_1h_1p_2p_2$-C_2 stereoisomer is also consistent with two methyl resonances and one ring proton resonance if rapid interconversion of the "square" and "diamond" faces of the bicapped trigonal prism persists at −161 °C.[19] Such interconversion can proceed via an *ssss* square antiprismatic transition state and requires only small atomic displacements.

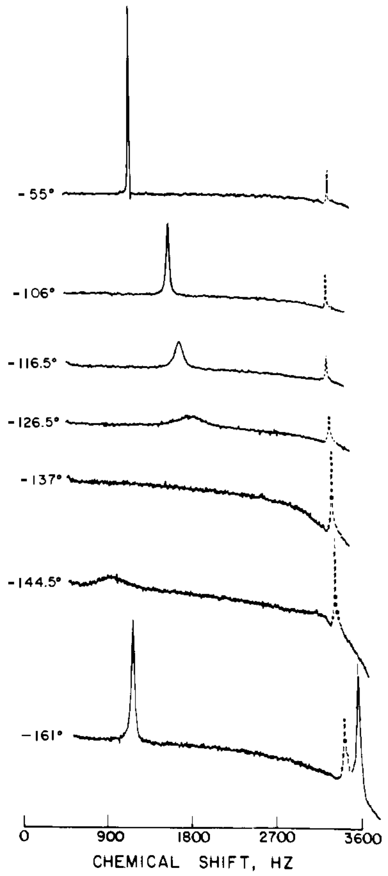

Figure 2. Methyl proton resonances for U(acac)$_4$ in 2:1 (v/v) CHClF$_2$/CH$_2$Cl$_2$ solution, 10 mg/mL, at 90 MHz. The relatively sharp resonance at high field, indicated by a broken line, is the 4.167-kHz upper side band of the ring proton resonance, and the sloping baseline at high field results from approach to the intense, out-of-phase, 4.167-kHz upper side band of the solvent resonance. The zero of the chemical shift scale is the methylene proton resonance of CH$_2$Cl$_2$.

Table I. Values of the Geometric Factor, $(3\cos^2\theta - 1)/r^3$ (Å^{-3}), for Protons in the More Probable Stereoisomers[a]

Stereoisomer	CH$_3$-A	CH$_3$-B	-CH=
mmmm-D_{2d}	0.0065	−0.0045	−0.0064
gggg-D_2 or S_4	0.0065	−0.0045	0.0047
ssss-D_2 (α = 0°)[b]	−0.0003	−0.0013	0.0030
ssss-D_2 (α = 4°)	−0.0008	−0.0018	0.0020
ssss-D_2 (α = 10°)	−0.0017	−0.0026	0.0004
$h_1h_1p_2p_2$-C_2 (α = 0°)	0.0006	−0.0017	0.0034
$h_1h_1p_2p_2$-C_2 (α = 9.5°)	−0.0008	−0.0028	0.0009

[a] Our calculations are based on averaged bond distances and angles in crystalline β-U(acac)$_4$[14] and α-Th(acac)$_4$.[22] [b] The angle α is the dihedral angle between the UO$_2$ plane and the C$_5$O$_2$ plane. Positive values of α correspond to a folding of the ligand portion of the ring away from the quasi-$\bar{8}$ axis.

Further evidence relating to the stereochemistry of U(acac)$_4$ in solution may be inferred from the signs of the isotropic paramagnetic shifts. Isotropic shifts, relative to the corresponding resonances of the diamagnetic Zr(acac)$_4$ complex, are upfield for the methyl protons (+8.0 ppm and +34.6 ppm at −155 °C) and downfield for the ring proton (−9.0 ppm and −155 °C). In view of the large isotropic shift between the two methyl resonances, it seems likely that the paramagnetic shifts are predominantly dipolar (pseudocontact) in origin.[20] Accordingly, we have calculated the geometric factor [$(3\cos^2\theta - 1)/r^3$][21] for the various protons of the more probable stereoisomers (cf. Table I). For the dodecahedral stereoisomers (*mmmm*-D_{2d}, *gggg*-D_2, and *gggg*-S_4), large dipolar shifts of opposite sign are predicted for the two acetylacetonate methyl groups. These predictions do not agree with experiment. For the idealized *ssss*-D_2 stereoisomer which has a D_{4d} square antiprismatic coordination polyhedron, the two acetylacetonate methyl groups would have the same geometric factor and therefore the same dipolar shift. However, distortion of the D_{4d} coordination polyhedron to a D_2 polyhedron by folding about one diagonal of each square face, as observed in crystalline Zr(acac)$_4$[12] and β-U(acac)$_4$,[14] results in different values of θ for the two acetylacetonate methyl groups. Calculated values (Table I) of the geometric factor for an *ssss*-D_2 stereoisomer having the D_2 coordination polyhedron found for crystalline β-U(acac)$_4$ predict dipolar shifts of the same sign for the two methyl groups and a dipolar shift of opposite sign for the ring proton. The relative magnitudes of the dipolar shifts for the methyl and ring protons depend upon whether or not the chelate ring folds about the *s* edges (O···O) of the polyhedron; however, the signs of the dipolar shifts for the methyl and ring protons remain opposite for chelate ring dihedral angles (α) of $\lesssim 11°$. Best quantitative agreement between the dipolar shifts and the calculated geometric factors is obtained for the $h_1h_1p_2p_2$-C_2 bicapped trigonal prismatic stereoisomer found in the α crystalline form, with a chelate ring folding angle of ~9.5°. The rings are folded away from the quasi-$\bar{8}$ axis as is observed in both α[22] and β[14] crystalline forms. Our results suggest, therefore, that U(acac)$_4$ exists in solution as the same $h_1h_1p_2p_2$ stereoisomer found in the α crystalline form and that the paramagnetic shifts are predominantly dipolar. The absolute sign of the shifts (upfield for CH$_3$, downfield for -CH=) indicates that $\chi_\parallel$ is greater than $\chi_\perp$.

Total line-shape analysis of the methyl resonances of U(acac)$_4$ between -157 (where $k = 69\ \mathrm{s}^{-1}$) and -106 °C (where $k = 2.8 \times 10^5\ \mathrm{s}^{-1}$) has afforded the following activation parameters for exchange of methyl groups between the two methyl environments: $\Delta H^* = 6.0 \pm 0.1$ kcal/mol, $\Delta S^* = 3.6 \pm 0.8$ eu, and ΔG^* (-110 °C) $= 5.43 \pm 0.04$ kcal/mol. For Zr(acac)$_4$, rate constants vary from 7.2 s^{-1} at -152 °C to 147 s^{-1} at -128 °C, and activation parameters are $\Delta H^* = 4.1 \pm 0.3$ kcal/mol, $\Delta S^* = -18.7 \pm 2.5$ eu, and ΔG^* (-110 °C) $= 7.18 \pm 0.06$ kcal/mol. These rearrangements are intramolecular as evidenced by the fact that exchange of acac ligands between the complexes and free acetylacetone is slow on the NMR time scale at temperatures (-50 °C for Zr(acac)$_4$ and -106 °C for U(acac)$_4$) above the coalescence region.

Ce(acac)$_4$ and Th(acac)$_4$ exhibit a single time-averaged methyl resonance at -169 °C, but limiting slow-exchange spectra have been observed for several other zirconium(IV) and uranium(IV) β-diketonates. For example, the ^{1}H spectrum of Zr(acac)$_2$(NO$_3$)$_2$ below -144 °C is consistent with the *mmmm*-C_2 dodecahedral structure found in the solid state,[23] and the ^{19}F spectrum of Zr(CF$_3$COCHCOCH$_3$)$_4$ at -155 °C indicates the presence of more than one stereoisomer. Our work in this area is continuing.

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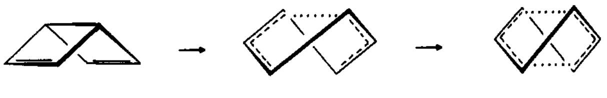
Thermolysis of Bicyclo[2.2.0]hexa-2,5-diene (Dewar Benzene)[1]

Sir:

The isomerization of Dewar benzene to benzene, apparently a symmetry-forbidden yet facile process, can be rationalized in various ways, some of them already published.[2] Independent experimental tests of such hypotheses are less common. We here report results of the first homogeneous gas phase thermolysis study of this precursor, of isotope labeling experiments that exploit its 1,2,4-trideuterio derivative, and of associated secondary deuterium kinetic isotope effect determinations. These severely restrict the useful range of continuing speculation.

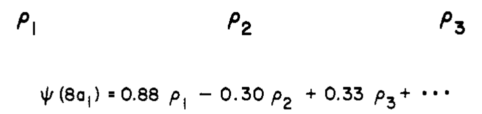
Isotopic scrambling of the precursor, for example, is suggested by two rather different hypotheses. One of them would replace the symmetry-forbidden $_\sigma 2_s + {}_\pi 2_s$ transformation by a spin-forbidden thermal crossing, initially to the lowest triplet state of the product.[2c,d] Experimentally, this triplet was detected through the fluorescence of 9,10-dibromoanthracene which it induces.[2c] The close correspondence between the observed $\Delta H^\ddagger$ (23 kcal/mol)[3] and the estimated $\Delta H°$ (≈ 25 kcal/mol)[2c] allows this first step also to be reversible and, hence, detectable by isotopic scrambling.

An earlier hypothesis provided a more topological escape from the pericyclic selection rule and a more explicit prediction of isotopic scrambling.[2b] Stretching of the central bond "accompanied by a quasi-conrotatory skewing distortion" (e.g., **1** → **1a**) would generate two mutually orthogonal allylic radicals, coupled only weakly and in an acyclic way across the residual bond. In retrospect, **1a** provides an alternative explanation for the subsequently discovered unsymmetrical substituent effects on reaction rate.[3,4] The weakly coupled allylic fragments can be stabilized by level splitting and by charge transfer. Isotopic scrambling becomes mandatory if distortion reaches the structure shown as **1b**, the "twist" transition state of a Cope rearrangement.[5]



1 1a 1b

An isotopically rearranged product instead is suggested by a third hypothesis and by its supportive experimental data.



ρ_1 ρ_2 ρ_3

$$\psi(8a_1) = 0.88\ \rho_1 - 0.30\ \rho_2 + 0.33\ \rho_3 + \cdots$$