sume that this is the same species originally used by Oppenauer[5] for oxidation of alcohols to aldehydes. However, when di-*tert*-butyl chromate, generated by Oppenauer's procedure, was employed in these oxidations under similar conditions (i.e., methylene chloride as solvent and in the presence of 1 equiv of pyridine) much poorer yields of aldehydes were obtained. Suga and coworkers have reported[6] that they were not able to reproduce the high yields described by Oppenauer even when following his procedure. It seems likely that the Oppenauer preparation of di-*tert*-butyl chromate was contaminated by the half ester. In any case, the present method is very convenient for rapid generation of the pure reagent.

In a typical experiment, a 1-l. round-bottom flask equipped with a dropping funnel, nitrogen inlet, thermometer, and magnetic or mechanical stirrer was charged with 300 ml of methylene chloride,[7] 20.6 ml of *tert*-butyl alcohol (220 mmol), and 26.6 ml of pyridine[7] (330 mmol) and was cooled to $-78°$ by means of a Dry Ice-acetone bath. To this solution 8.9 ml of chromyl chloride[8] (110 mmol) in 50 ml of carbon tetrachloride[7] was added by dropping funnel over a period of 15 min so that the temperature did not exceed $-70°$. The reaction mixture was allowed to warm to room temperature at which point the solution was red-orange and a white precipitate of pyridine hydrochloride was apparent. A solution of 15.8 g (100 mmol) of 1-decanol in 100 ml of methylene chloride was added all at once. The solution turned brown immediately and was stirred for 2 hr; there is surprisingly little heat released during this stage of the reaction. At this point 1 ml of dimethyl sulfide was added to destroy any unreacted chromium(VI) species. The reaction mixture was concentrated to ca. 100-200 ml and poured into 500 ml of ether. A brown precipitate separated and the flask was swirled frequently for 30 min to complete the precipitation. The organic phase was decanted and the precipitate was washed twice with 100-ml portions of ether. The combined organic layer was washed twice with 500-ml portions of 5% NaOH, 5% HCl, 5% $NaHCO_3$, and saturated NaCl and dried over Na_2SO_4. The solvent was removed and the residue was filtered[9] through a very short column of silica gel (2 cm^3) with pentane to remove the last traces of chromium salts. Distillation afforded 13.1 g (84%) of 1-decanal bp 65-67° (3 mm), which was >98% pure by GLC. This same procedure when carried out on a 500 mmol scale gave a 79% distilled yield of 1-decanal.

Ratcliffe has carried out the oxidation of 1-decanol on a 100 mmol scale using the modified Collins reagent and obtained a 63-66% distilled yield of 1-decanal.[10] In addition to more chromium the Collins procedure also requires greater solvent volumes (1600 vs. 450 ml) than the method described above.

It is apparent that this new method is inferior to the Collins oxidation for allylic alcohols such as geraniol since cis-trans isomerization occurs. We have also noted that reagent **5** has more of a tendency to perform allylic oxidations than does reagent **1**. In general this new reagent (**5**) is less selective than the Collins reagent (e.g., 3-hydroxybenzyl alcohol gives a very poor yield of the hydroxy aldehyde which is obtained in good yield with reagent **1**). However, for large scale oxidations of simple saturated[11] primary alcohols to aldehydes this new method should offer advantages over existing procedures.

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(8) Chromyl chloride was prepared according to the procedure described in Brauer's "Handbook of Preparative Inorganic Chemistry," Vol. 2, Academic Press, New York, N.Y., 1965, p 1384. The chromyl chloride available from ROC/RIC and Alfa works equally well and was used without purification.
(9) If this step is omitted the distilled yield drops by 5–10%. However, when distillation is not required, this filtration is probably not necessary.
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(12) Camille and Henry Dreyfus Teacher–Scholar grant recipient; Alfred P. Sloan Fellow, 1973–1975.

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Dynamic Nuclear Magnetic Resonance Studies of Inversion and Diketonate R-Group Exchange in Dialkoxybis(β-diketonato)titanium(IV) Complexes

Sir:

The utility of diastereotopic groups[1] in investigations of the kinetics and mechanism of intramolecular rearrangements of chiral metal chelates has been demonstrated by several recent dynamic NMR (DNMR) studies.[2-4] A simple and potentially fruitful approach in mechanistic studies of stereochemically nonrigid chelate complexes involves comparison of the rate of inversion of configuration, probed by the diastereotopic groups, and the rate of some other metal-centered process, for example, exchange of terminal substituents on AA chelate rings in mixed-ligand complexes of the type $M(AA)_2(BB)$.[4] We present herein a preliminary report of our DNMR studies of inversion and terminal group exchange in the octahedral dialkoxybis(β-diketonato)titanium(IV) complexes **1–6** (Table I[5]). These two processes occur simultaneously and at comparable rates by a common, intramolecular mechanism; the relative rate of inversion and terminal group exchange, $R_k = k_{inv}/k_{ex}$, decreases from ~2.0 to ~1.0 with increasing steric bulk of the alkoxide ligand. The dependence of the absolute rates and activation enthalpies on the bulk of the alkoxide ligand suggests that these complexes rearrange by a twist mechanism (vide infra). We are prompted to report our results at this time by a preliminary account of DNMR studies of some closely related glycollatobis(acetylacetonato)titanium(IV) complexes.[6]

Complexes **1–6** belong to the dissymmetric point group C_2. Consequently the alkoxide geminal hydrogen atoms and geminal methyl groups are diastereotopic. At low temperatures the ^1H NMR spectra show two alkoxide methyl resonances for compounds **3** and **6**, two isopropoxide methyl doublets for **2**, an AB pattern for the methylene protons of **4**, and the AB part of an ABX pattern for the methylene

Table I. Kinetic Data for Some Dialkoxybis(β-diketonato)titanium(IV) Complexes[a]

Compound	Process	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	$k_{25°}$, sec^{-1}	$\Delta G^\ddagger$, kcal/mol (T_c,[b] °C)	k, sec^{-1} ($\sim T_c$, °C)	$R_k = k_{inv}/k_{ex}$ at $\sim T_c$
1 $Ti(acac)_2(OCH_2CH(CH_3)_2)_2$	Inversion	11.8 ± 0.5	−11.4 ± 1.8	41.3	15.19 ± 0.07 (20)	26.9 ± 3.2 (19)	2.09 ± 0.4
	Exchange	11.6 ± 0.7	−13.9 ± 2.4	19.6	15.61 ± 0.07 (19)	12.9 ± 1.7 (19)	
2 $Ti(acac)_2(OCH(CH_3)_2)_2$	Inversion	14.0 ± 0.7	−6.2 ± 2.3	15.8	15.76 ± 0.07 (15)	12.3 ± 1.5 (22)	1.78 ± 0.3
	Exchange	14.1 ± 0.3	−6.8 ± 1.1	8.9	16.19 ± 0.05 (29)	6.9 ± 0.6 (22)	
3 $Ti(acac)_2(OC(CH_3)_2C_6H_5)_2$[c]	Inversion	15.3 ± 0.4	−7.2 ± 1.3	1.01	17.59 ± 0.06 (45)	12.7 ± 1.2 (56)	1.41 ± 0.2
	Exchange	15.2 ± 0.4	−8.3 ± 1.2	0.73	17.99 ± 0.05 (67)	9.0 ± 0.7 (56)	
4 $Ti(dpm)_2(OCH_2C_6H_5)_2$	Inversion	11.7 ± 0.4	−12.2 ± 1.5	32.5	15.33 ± 0.05 (20)	45.9 ± 3.8 (30)	1.64 ± 0.2
	Exchange	12.1 ± 0.3	−12.2 ± 1.1	19.7	15.80 ± 0.06 (34)	28.0 ± 2.6 (30)	
5 $Ti(dpm)_2(OCH_2CH(CH_3)_2)_2$	Inversion	13.9 ± 0.8	−6.4 ± 2.6	17.4	15.78 ± 0.05 (28)	26.0 ± 2.7 (30)	1.37 ± 0.2
	Exchange	13.5 ± 0.3	−8.2 ± 1.0	12.8	16.01 ± 0.05 (33)	19.0 ± 1.6 (30)	
6 $Ti(dpm)_2(OC(CH_3)_2C_6H_5)_2$[c]	Inversion	16.9 ± 0.9	−9.3 ± 2.5	0.023	20.20 ± 0.07 (82)	9.2 ± 1.0 (100)	1.06 ± 0.2
	Exchange	17.1 ± 0.5	−8.8 ± 1.3	0.020	20.57 ± 0.08 (119)	8.7 ± 0.9 (100)	

[a] In $CDCl_3$ unless indicated otherwise. All errors are random errors estimated at the 95% confidence level. [b] Coalescence temperature. [c] In 1,1,2,2-tetrachloroethane.

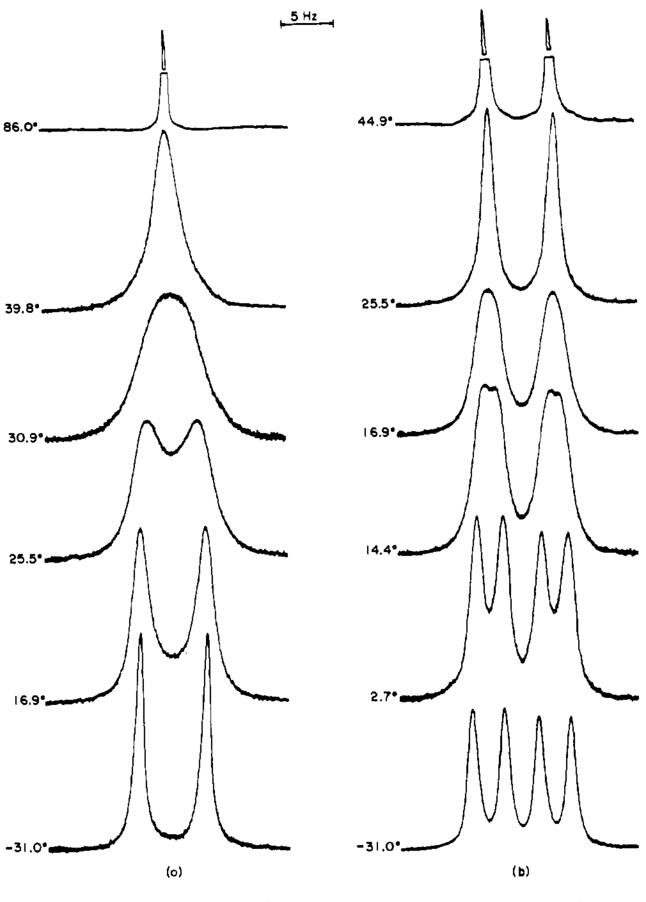

Figure 1. DNMR spectra of $Ti(acac)_2(OCH(CH_3)_2)_2$ in $CDCl_3$ solution: (a) acac methyl resonances; (b) isopropoxide methyl resonances.

protons of **1** and **5**. These signals coalesce at higher temperatures to give a single, time-averaged resonance for compounds **3**, **4**, and **6**, and a single, time-averaged doublet for **1**, **2**, and **5**. We interpret these coalescence processes in terms of exchange of the diastereotopic groups owing to inversion of configuration at the metal center.

DNMR spectra of **2** have been investigated previously by three research groups.[6-8] The earlier workers[7,8] attributed the two isopropoxide methyl doublets to restricted rotation. However, Baggett et al.[6] have correctly pointed out that the geminal methyl groups are diastereotopic for symmetry reasons even when rotation is free. Accordingly, we find that the unhindered mixed-ligand complex $Ti(dpm)_2(OCH_2C_6H_5)Cl$ exhibits an AB pattern for the methylene protons.

At low temperatures, the terminal R groups on the β-diketonate ligands of **1-6** give two equally intense methyl (or *tert*-butyl) resonances. These coalesce to a single, time-averaged resonance in approximately the same temperature range in which inversion causes coalescence of the alkoxide resonances. Typical spectra are presented in Figure 1.

Rate constants for inversion and diketonate R-group exchange (Table I) were determined by total line-shape analysis, taking into account the temperature dependence of the relaxation times and, when appropriate, the temperature dependence of the chemical shift in the absence of exchange. The following evidence indicates that inversion and R-group exchange occur by a common, intramolecular mechanism. (1) For all compounds studied, these two processes have comparable rates ($1.0 \leq R_k \leq 2.0$; cf. Table I) and essentially identical activation parameters. (2) The rates are independent of concentration and are nearly independent of the solvent. (3) Intermolecular ligand exchange between the complex and free diketone or free alcohol is slow on the NMR time scale at temperatures where inversion and R-group exchange are fast.

Certain intramolecular mechanisms may be ruled out as the sole rearrangement pathway on the basis of the observed values of R_k, which vary from ~2.0 to ~1.0 with increasing steric bulk of the alkoxide ligand. For example, rearrangement via trigonal-bipyramidal-axial (TBP-axial) and TBP-equatorial five-coordinated intermediates with a monodentate β-diketonate ligand requires $R_k \geq 2.0$ and $R_k = 0$, respectively, while twists about a single octahedral C_3 axis[9] predict $R_k = 1.0$ or $R_k = 2.0$, depending on the C_3 axis about which the twist occurs. A detailed analysis of the value of R_k expected for various mechanistic possibilities indicates that the observed variation in R_k requires a mixture of two (or more) mechanisms, with the relative contribution of each depending on the steric bulk of the alkoxide ligand.

Bradley and Holloway[7] have earlier noted that the barrier to R-group exchange in $Ti(acac)_2(OR)_2$ complexes seems to increase in the series R = CH_3, C_2H_5, i-C_3H_7, t-C_4H_9, and they have suggested that this steric effect favors a twist over a bond-rupture mechanism. Strong support for a twist mechanism is provided by the rather more dramatic steric effects evident in Table I; for the $Ti(dpm)_2(OR)_2$ complexes, $k_{25°}$ decreases by ~10^3 and $\Delta H^\ddagger$ increases by 5 kcal/mol on going from a primary alkoxide (OR = $OCH_2C_6H_5$) to a tertiary alkoxide (OR = $OC(CH_3)_2C_6H_5$). The variation in R_k can be accounted for in terms of a sterically induced variation in the relative amount of twisting about the various octahedral C_3 axes. Additional evidence against a bond-rupture mechanism is afforded by our NMR studies of the cationic tris chelates $Ti(bzac)_3^+$, $Ti(bzac)_2(bzbz)^+$, and $Ti(acac)_2(bzbz)^+$.

These cations should contain stronger Ti–O bonds than the electrically neutral $Ti(dik)_2(OR)_2$ complexes; yet the cations are nonrigid on the NMR time scale at −105°. The question of bond rupture vs. twisting is not settled by the NMR spectrum of the triacetylmethanate (triac) complex studied by Baggett et al.[6] since internal rotation in the partly dissociated triac ligand probably is slow at 35°; for $Co(triac\text{-}d_3)_3$, linkage isomerization is nine times slower than inversion at 105.2° and $\Delta H^\ddagger$ for linkage isomerization is higher by 8 kcal/mol.[10]

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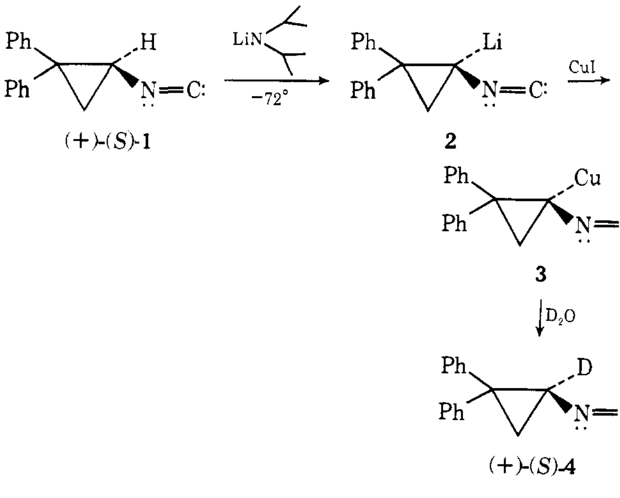
Cyclopropane. XXXVII. A Stable Chiral Copper Reagent[1]

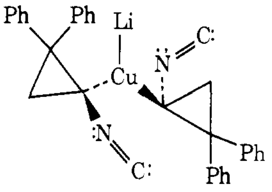
Sir:

In general, organocopper reagents are stereochemically unstable at ambient temperatures. This seems to be the case whether the copper is bound to an sp^3 or sp^2 carbon atom or whether or not the copper(I) is coordinated to stabilizing ligands.[2,3] We wish to report on the preparation of the first optically stable copper(I) reagent in which the copper(I) is directly attached to the chiral center.[4]

Recently[5] we reported that 1-lithio-1-isocyano-2,2-diphenylcyclopropane (**2**), generated from chiral (+)-(*S*)-1-isocyano-2,2-diphenylcyclopropane (**1**) by reaction with lithium diisopropylamide, is capable of maintaining its configuration at temperatures between −52 and −72° but racemizes at −5°. Treatment of **2**, formed at −72° in tetrahydrofuran, with cuprous iodide and allowing the temperature to slowly rise[6] to 10° over a period of 30 min produced **3**. The reaction mixture was hydrolyzed with water to regenerate (+)-(*S*)-**1** in 20% yield[7] and an optical purity of 95%. In another experiment the reaction mixture was quenched with deuterium oxide to yield (+)-(*S*)-**4** (16% yield)[7] with retention of configuration (98% optical purity) and 90 ± 1% deuterium incorporation. The configurational stability of **3** was unaffected by an increase in temperature and length of reaction time. For example, addition of cuprous iodide to **2** at −70° and allowing the reaction mixture to warm up to room temperature (23°) over a period of 30 min followed by deuterium oxide deuterolysis yielded (+)-(*S*)-**4** (70% yield)[6] with an optical purity of 91% and with 89% deuterium incorporation. Repeating this experiment but changing the reaction time from 30 min to 2 hr did not affect the stereochemistry nor the amount of deuterium incorporation. Based on these data it is concluded that **3** represents the first stable chiral organocopper(I) compound having an asymmetric carbon atom directly attached to copper(I).



We have observed that the addition of either 1 equiv of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), 2 equiv of triglyme, or 2 equiv of 15-crown-5 to a tetrahydrofuran solution of **2** at −72° did not affect the configurational stability.[8] Also, in the case of **3**, the addition of TMEDA at 23° for 30 min did not alter the stereochemical behavior but the addition of crown ether did have an effect. Thus, to a tetrahydrofuran solution of **3** at 23° 1 equiv of TMEDA was added, stirred for 30 min, and quenched with deuterium oxide to give **4** in 84% yield. The optical purity was found to be 94% and the deuterium incorporation was 95%. However, when the reaction was carried out using 1 equiv of 15-crown-5 a mixture of **1** and **4** was isolated (40% yield) with an optical purity of 88% and a deuterium content of 70%. Moreover, if the reaction time was increased to 12 hr at 23°, the optical purity of the product (20% yield) was reduced to 68% and the deuterium content was very low,[9] 19%.



5

The chiral cuprate (I) **5** has also been prepared by the addition of 0.5 equiv of cuprous iodide to 1 equiv of **2** at −72° and allowing the temperature to rise to −5° over a period of 30 min.[6] Quenching the reaction mixture with deuterium oxide yielded **4** which was 97% optically pure with 33% deuterium incorporated. However, if the reaction is run at 10° and then quenched with deuterium oxide the deuterium content of **4** remains the same but the optical purity is decreased to 70%.

A comparison of the optical stabilities of **2**, **3**, and **5** indicates that the order of stability is **3** > **5** > **2**. Further studies on the configurational stabilities of isocyano carbanions are in progress.

References and Notes

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