ular process involving one or two CH_3OH^* molecules which is not intercepted even by 0.1 M $FeCl_3$.

Generation of CH_3OH^* can be ascribed to energy released by recombination of $N(^4S)$ atoms, a process which in the gas phase proceeds largely via $N_2(A^3\Sigma_u^+)$.[13] Methanol is known to quench the latter species in the gas phase.[14] Analogous gas phase quenching of $N_2(A^3\Sigma_u^+)$ leads to the decomposition of H_2,[15,16] CO_2,[16] N_2O,[16] and NH_3.[17] The total energy released on recombination of nitrogen atoms is 225 kcal/mol. Either this energy or the 142 kcal/mol of the 0 vibrational level of $N_2(A^3\Sigma_u^+)$ is more than sufficient to bring about the decomposition of the methanol molecule. We wish to suggest that energy released on recombination of nitrogen atoms induces decomposition of methanol in localized regions not unlike the "spur" regions which are well known in radiolysis of water.[18] Spin selection rules and energetic considerations respectively militate against insertion and abstraction reactions of nitrogen atom. Its reactions with saturated substrates in condensed phase are apparently governed by the process described above. This chemistry is unusual, and perhaps unique, among atomic reagents.

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Oxidation of Alcohols to Aldehydes by Reagents Derived from Chromyl Chloride

Sir:

The Collins oxidation[1] and its modification by Ratcliffe[2] are among[3] the most reliable procedures for the oxidation of a saturated primary alcohol to its corresponding aldehyde. An unfortunate aspect of these chromium trioxide-pyridine based reagents is that about 6 equiv of oxidant are needed to ensure rapid and complete oxidation. It is apparent that this requirement for excess oxidant is due, at least in part, to the production of water during the course of the oxidation (eq 1). Collins had previously shown[1] that reagent **1** reacts rapidly with water to produce the insoluble pyridinium dichromate **3**. The basic chromium dioxide species **2** is also likely to coordinate with, and deactivate, further quantities of reagent **1**. We reasoned that both of these problems might be overcome if chlorine were the hydrogen acceptor rather than oxygen. In support of these arguments we have found that when chromyl chloride (CrO_2Cl_2, **4**) is used in place of chromium trioxide 1.1 equiv of reagent are sufficient to effect complete oxidation.

Table I. Per Cent Yield[a] of Aldehyde or Ketone

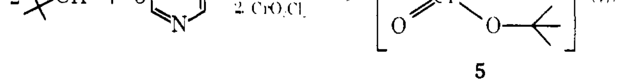
Alcohol	Moles	% CrO_2Cl_2[b]	% **5**[c]
1-Decanol	0.1	—	84
	0.5	—	79
1-Dodecanol	0.01	94	99
Citronellol	0.01	87	93
	0.1	—	84
Geraniol	0.01	87[d]	100[d]
2-Methyl-2-phenyl-propanol	0.1	—	86
Benzyl alcohol	0.01	85	100
Cyclohexane methanol	0.01	90	99
Cyclododecanol	0.01	99	97
Cinnamyl alcohol	0.01	78	86
Pinocarveol	0.01	82	60
3-Hydroxy benzyl alcohol	0.01	0	38

[a] The yields of the small scale reactions (0.01 mol) were determined by GLC relative to an internal standard; all other yields (i.e., 0.1 and 0.5 mol) are for distilled pure substances. [b] These reactions were all carried out on a 10 mmol scale, and the procedure is the same as that described for the use of reagent 5 for oxidation of 1-decanol on a 0.1 mol scale with the exception that *tert*-butyl alcohol was omitted and that 4 rather than 3 equiv of pyridine was used. [c] All these oxidations were carried out exactly as described for the oxidation of 0.1 mol of 1-decanol. However, on the 0.01 mol scale it is not necessary to dilute the CrO_2Cl_2 with CCl_4 prior to addition. [d] Z–E isomerization occurs and one obtains a 3:1 mixture of geranial and neral.

$$\underset{\mathbf{1}}{CrO_3 \cdot 2pyr} + RCH_2OH \rightarrow \underset{\mathbf{2}}{CrO_2 \cdot 2pyr} + RCHO + H_2O \qquad (1)$$

$$\mathbf{1} + H_2O \rightarrow \underset{\mathbf{3}}{Cr_2O_7^{2-}(pyr\,H^+)_2} \qquad (2)$$

When chromyl chloride is added to a solution of pyridine in methylene chloride cooled in a Dry Ice-acetone bath, a red-brown slurry is produced.[4] The alcohol is added to this slurry and rapid oxidation ensues even at −70°. The reaction mixture is allowed to warm to ambient temperature and good to excellent yields of aldehydes are realized (see Table I under CrO_2Cl_2). Unfortunately, this oxidation is so vigorous that it is difficult to control on a scale much larger than 10 mmol. In order to overcome this problem the reagent was modified further by addition of *tert*-butyl alcohol (eq 3). The reagent (**5**) thus produced is remarkably effective for these oxidations on both small and large scales (see Table I under reagent **5**). Since reagent **5** is probably di-*tert*-butyl chromate, or its pyridine adduct, one might as-



(3)

5

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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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