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Partial Photoresolution. IV. *cis*- and *trans*-Tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III) Photoisomerization and Inversion at 5461 Å in Chlorobenzene Solution

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Abstract: The partial resolution of both *cis*- and *trans*-tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III) was accomplished in chlorobenzene solution by irradiation with circularly polarized light at 5461 Å. Because photoisomerization accompanied inversion, the cis and trans isomers were separated by tlc. The circular dichroism spectra, normalized to optically pure enantiomer, yielded maxima at 615 and 430 nm and a minimum at 545 nm. The only significant difference between the CD spectra is that the values of $(\epsilon_l - \epsilon_r)$ at the 545- and 615-nm bands are more positive for the trans isomer. This discrepancy is justified stereochemically. Quantum yields were obtained for the six possible transformations in the cis–trans system, *i.e.*, inversion of either geometrical isomer without isomerization, inversion of either isomer with isomerization, and isomerization of either isomer without inversion. The results indicate that all processes occur, suggesting that both bond-rupture and twisting mechanisms are present.

Partial photoresolution or the process of inducing optical activity in a racemic mixture by causing a photolytic inversion of enantiomers has been applied successfully to Cr(III) complexes with oxalato,[1-3] ethylenediamine,[4] 1,10-phenanthroline, and 2,2'-bipyridine,[5] and acetylacetonato[6] ligands. In the Cr(acac)$_3$ case, the reaction quantum yields in various organic solvents were smaller than for Cr(ox)$_3^{3-}$ in aqueous solution by factors of 50 or so,[6] suggesting perhaps that the photolysis mechanism of the former is quite different from that of the latter, which is assumed to invert through a water catalyzed bond-rupture process.[7]

The tris(1,1,1-trifluoro-2,4-pentanedionato)chromium-(III), or Cr(tfa)$_3$, system, while being chemically very similar to Cr(acac)$_3$, should yield more information concerning the mechanism(s) of inversion because of the fact that a geometrical isomerization may occur simultaneously with the optical inversion as a result of the unsymmetrical ligand. This gives rise to the photokinetic system shown in Figure 1. Because certain mechanisms, *e.g.*, trigonal twist, rhombic twist, bond rupture with trigonal-bipyramid intermediate, etc., are allowed by only certain pathways, **1** through **6**, a knowledge of values of the six quantum yields

should give some insight into the preferred mechanism(s).

In addition to photokinetic information, a photoresolution yields the ORD and CD spectra of optically pure enantiomers, which have not been hitherto obtained by other workers. Sometimes it is assumed in studies of systems of complexes like this one that the cis and trans isomers have the same rotational strengths, and so another reason for this study was to test the validity of such an assumption.

Experimental Section

The compound Cr(tfa)$_3$ was prepared according to an established procedure.[8] The cis and trans isomers were completely separated on 1000-μ, 20 × 20 cm, tlc plates (Analtech silica gel G) using 50:50 v/v benzene–hexane for the developing solvent. The slower moving fraction, which was less abundant, was assumed to be the cis isomer because of similar results obtained by Fay and Piper on liquid columns.[9] The R_f factors are about 0.33 and 0.16 for the trans and cis isomers, respectively. In order to increase the amount of cis isomer, the purified trans isomer was dissolved in o-dichlorobenzene and refluxed for several hours after which the tlc fractionation procedure was repeated. *Anal.* Calcd for Cr(CF$_3$COCHCOCH$_3$)$_3$: C, 35.22; H, 2.35; F, 33.46. Found:
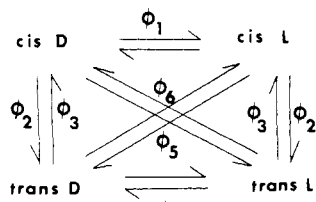
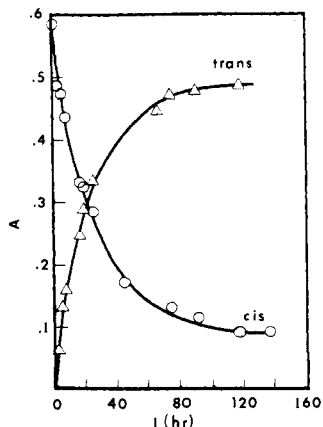Figure 1. The photokinetic reaction system.

Figure 2. The absorbance of cis and trans fractions at 567 nm after 2:1 dilution as a function of irradiation time in 5461 Å light (200-W system) in an initially 0.02 M cis-Cr(tfa)$_3$ solution.

(trans) C, 35.11; H, 2.35; F, 33.66; (cis) C, 35.48; H, 2.33; F, 33.32.

Solutions of about 0.02 M complex in chlorobenzene were prepared and stored in a refrigerator until use. One-half-milliliter samples were placed in 1-cm glass cuvettes thermostated to 34 ± 0.1° and irradiated with left-handed circularly polarized light at 5461 Å. The lamp used was either a 200-W Osram mercury high-pressure lamp (HBO-200W) or a 1000-W Hanovia mercury-xenon high-pressure lamp (977B-1). The light intensity was measured periodically using the potassium reineckate actinometer system,[10] and it was observed that during the course of a run the light intensity never varied by more than 3%.

A typical run consisted of irradiating about nine 0.5-ml samples of initially pure cis or pure trans solutions for suitable times in an optical system described previously,[2] taking an ORD curve on the sample between 600 and 475 nm with a Bendix spectropolarimeter, fractionating the sample on a 250-μ, 5 × 20 cm tlc plate, eluting the fractions, drying, and dissolving to 1 ml in chlorobenzene, and measuring absorbance at 567 nm and ORD of both fractions. Although there was always a slight loss in total sample after the fractionation step, the absorbance and ORD readings could be normalized to corrected values by multiplying by either (total absorbance before)/(total absorbance after), or (total ORD before)/(total ORD after fractionation).

The CD spectra were measured on a Cary 60 spectrometer, and the absorption spectra were taken on a Bausch and Lomb Spectronic 505 spectrometer.

Results and Discussion

I. Optical Activity. Figures 2 and 3 illustrate the approach to the photostationary state in an initially cis sample for both cis and trans fractions. Figure 2 shows the absorbance of the fractions at 567 nm as a function of time, and Figure 3 shows the optical activity ($\alpha_{max} - \alpha_{min}$) of the two fractions.

The assumption that at the photostationary state the D and L forms of either cis or trans isomer absorb the same amount of circularly polarized light (vida infra) leads to the same relationships as occur in the case of a trigonal complex with symmetric ligands,[2] namely

$$(A_1 - A_r)_{pss} = C(g/2)(\epsilon_1 - \epsilon_r)$$
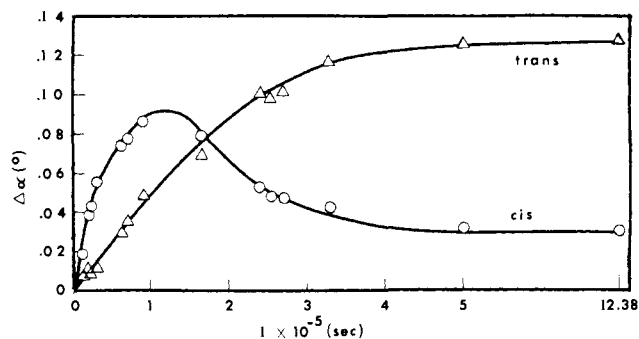

Figure 3. The ORD amplitude of cis and trans fractions as a function of irradiation time in 5461 Å LCP light (200-W system) in an initially 0.02 M cis-Cr(tfa)$_3$ solution.

Table I. Optical Activity

Isomer	C_{pss}, M	$\alpha_{max} - \alpha_{min}$	$(\epsilon_1 - \epsilon_r)_{5461}$
cis-Cr(tfa)$_3$	$3.3 \times 10^{-3} \pm 5\%$	$-0.0269 \pm 5\%$	-4.4 ± 0.2
$trans$-Cr(tfa)$_3$	$1.7 \times 10^{-2} \pm 5\%$	$-0.114 \pm 5\%$	-3.9 ± 0.2

where $(A_1 - A_r)_{pss}$ is the observed circular dichroism of cis or trans fraction at the photostationary state, C is the photostationary-state concentration of the isomer in the fraction, g is the dissymmetry factor $(\epsilon_1 - \epsilon_r)/\epsilon$, and ϵ_1, ϵ_r, and ϵ are the decadic absorption coefficients in left, right, and nonpolarized light, respectively. Table I displays the average values of quantities obtained from six photostationary-state samples, using both 200- and 1000-W lamp systems. From these quantities, the values of $(\epsilon_1 - \epsilon_r)$ at 5461 Å for either isomer were calculated and are shown in Table I. From these values, the normalized ORD and CD spectra were constructed from spectra taken on partially resolved samples.

The normalized spectra are shown in Figure 4 for the cis and trans complexes. They are very similar to the spectra of the tris(acetylacetonato)chromium complex,[6] exhibiting three CD bands in the visible region, although the CD bands at 430 nm are rather more like shoulders than clean bands as in the case of Cr(acac)$_3$. Although the absorption spectra are identical, the most interesting difference between the CD spectra of the cis and trans isomers is that the band at about 540 nm has a larger negative magnitude for the cis than the trans (-4.4 vs. -4.0), whereas the band at 615 nm is larger for the trans than for the cis (2.2 vs. 1.1). The splitting of an absorption band in an octahedral complex into two CD bands of opposite sign in a corresponding trigonal complex has been described by Mason[11] as resulting from the fact that the chiral perturbations on the metal chromophore are of opposite chirality, one acting along the C_3 axis of the trigonal complex and the other acting along the C_2 axis. If the CD band at 540 nm is associated with the C_3 or pseudo-C_3 axis of either cis- or $trans$-Cr(tfa)$_3$ (see Figure 5), it can be seen that the chiral environment about this axis is greater for the cis than the trans, thus giving rise to a larger magnitude of CD for the cis isomer. Similarly, the trans isomer exhibits a greater chirality about its pseudo-C_2 axis than does the cis isomer, resulting in a larger CD for the trans at 615 nm.

II. Photokinetics. The system in Figure 1 gives rise to a set of photochemical rate equations such as eq 1 where ϕ is the quantum yield and J[12] is the molar light absorption

$$\frac{d[cis\ D]}{dt} = \phi_1(J_{cL} - J_{cD}) -$$

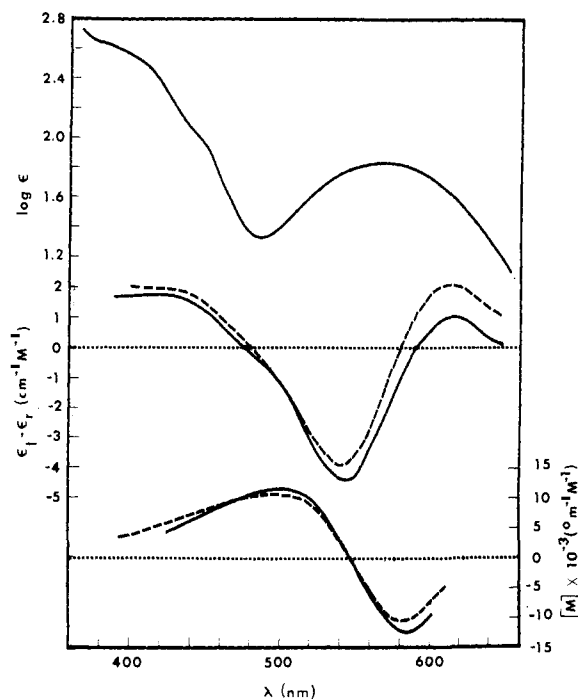$$(\phi_2 + \phi_5)J_{cD} + \phi_3 J_{tD} + \phi_6 J_{tL} \quad (1)$$

Figure 4. Visible absorption, circular dichroism, and ORD spectra of chlorobenzene solutions of $(-)$-cis-$Cr(tfa)_3$, (——); and $(-)$-trans-$Cr(tfa)_3$, (-----).

Figure 5. Views of Δ configurations of cis- and trans-$Cr(tfa)_3$ (a) along C_3 or pseudo-C_3 axis and (b) along pseudo-C_2 axis.

Table II. Photoisomerization Quantum Yields

Initial isomer	$10^6 I_0$, einsteins $l.^{-1} sec^{-1}$	Rate law	$10^4(\phi_3 + \phi_6)$
Cis	15.2	Integrated	$9.3 \pm 6\%$
Trans	15.2	Integrated	$9.4 \pm 10\%$
Cis	3.9	Differential	$10.4 \pm 10\%$
Trans	2.2	Differential	$8.0 \pm 20\%$

rate in einsteins $l.^{-1} sec^{-1}$. Since the reactions are followed by observing the induced optical activity and absorbance of tlc fractions, it is useful to combine the set of equations as in eq 1 into another set which expresses rates of change of [cis D] − [cis L] and [trans D] + [trans L], which are proportional to optical activity, and [cis D] + [cis L] and [trans D] + [trans L], which are proportional to absorbance. One thus obtains eq 2a, 2b, and 3. Equations 2 can be referred to

$$\frac{d\{[\text{cis D}] - [\text{cis L}]\}}{dt} =$$
$$(\phi_3 - \phi_6)(J_{tD} - J_{tL}) - (2\phi_1 + \phi_5)(J_{cD} - J_{cL}) \quad (2a)$$

$$\frac{d\{[\text{trans D}] - [\text{trans L}]\}}{dt} = (\phi_2 - \phi_5)(J_{cD} - J_{cL}) -$$
$$(2\phi_4 + \phi_3 + \phi_6)(J_{tD} - J_{tL}) \quad (2b)$$

$$\frac{d\{[\text{cis D}] + [\text{cis L}]\}}{dt} = \frac{-d\{[\text{trans D}] + [\text{trans L}]\}}{dt} =$$
$$(\phi_3 + \phi_6)(J_{tD} + J_{tL}) - (\phi_2 + \phi_5)(J_{cD} + J_{cL}) \quad (3)$$

as the photoresolution rate laws, and eq 3 is the photoisomerization rate. Assuming that the principle of microscopic reversibility of states[13] applies to this system in the photostationary state, each reversible pair of reactions in Figure 1 will be in equilibrium. This allows for the determination of $\epsilon_l - \epsilon_r$ for cis and trans isomers in part I. In terms of the photoisomerization, it means that

$$\frac{\phi_3}{\phi_2} = \frac{\phi_6}{\phi_5} = \frac{\phi_3 + \phi_6}{\phi_2 + \phi_5} \quad (4)$$

Since eq 3 is equal to 0 at the photostationary state one obtains eq 5. Equation 3 can be used to find $\phi_3 + \phi_6$ and $\phi_2 +$

$$K = \frac{\phi_3 + \phi_6}{\phi_2 + \phi_5} =$$
$$\frac{(J_{cis})_{pss}}{(J_{trans})_{pss}} = \frac{(A_{cis})_{pss}}{(A_{trans})_{pss}} = \frac{[\text{cis}]_{pss}}{[\text{trans}]_{pss}} \quad (5)$$
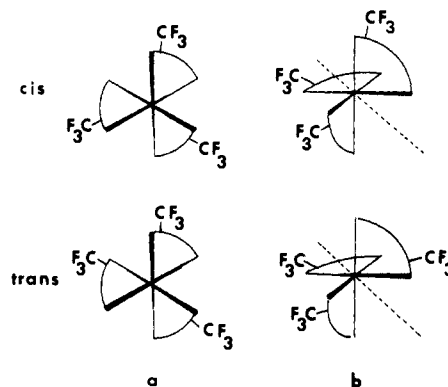
ϕ_5 by the method of initial rates, or it can be integrated to yield the useful expressions for initially cis (eq 6a) and ini-

$$\frac{-K}{K + 1} \frac{\ln (C_0 - K[\text{trans}] - [\text{trans}])}{C_0/K} =$$
$$\frac{I_0(1 - 10^{-A})}{A} \epsilon(\phi_3 + \phi_6)t \quad (6a)$$

$$\frac{-K}{K + 1} \frac{\ln (K[\text{trans}] + [\text{trans}] - C_0)}{C_0 K} =$$
$$\frac{I_0(1 - 10^{-A})}{A} \epsilon(\phi_3 + \phi_6)t \quad (6b)$$

tially trans (eq 6b), where $C_0 = [\text{cis}] + [\text{trans}]$ and $\epsilon = $ molar absorption coefficient of either isomer (both of which are the same) at the irradiating wavelength. The slopes of suitable plots as indicated by these equations will yield values of $\phi_3 + \phi_6$. Table II indicates the values obtained for the photoisomerization quantum yields and the methods employed. Based on these results, the value of 9.3×10^{-4} was used for $\phi_3 + \phi_6$, which gives a value of 4.9×10^{-3} for $\phi_2 + \phi_5$ since $K = 0.196 \pm 5\%$.

The photoresolution equations, 2, are not integrable, but they can be expanded into four initial rate equations by assuming that at the start of the reaction, only one geometrical isomer absorbs light. Thus one obtains for initially cis complex

$$\frac{d\{[\text{cis D}] - [\text{cis L}]\}}{dt} =$$
$$-(2\phi_1 + \phi_2 + \phi_5)(J_{cD} - J_{cL}) \quad (7a)$$

$$\frac{d\{[\text{trans D}] - [\text{trans L}]\}}{dt} = (\phi_2 - \phi_5)(J_{cD} - J_{cL}) \quad (7b)$$

and for initially trans complex

$$\frac{d\{[\text{cis D}] - [\text{cis L}]\}}{dt} = (\phi_3 - \phi_6)(J_{tD} - J_{tL}) \quad (7c)$$

$$\frac{d\{[\text{trans D}] - [\text{trans L}]\}}{dt} =$$
$$-(2\phi_4 + \phi_3 + \phi_6)(J_{tD} - J_{tL}) \quad (7d)$$

In order to recast these expressions into ones utilizing the measurable parameter, $\Delta A = A_{\rm l} - A_{\rm r}$,[14] one needs to recognize the following

$$\Delta A_{\rm cis} = \{[{\rm cis\ D}] - [{\rm cis\ L}]\}(\epsilon_{\rm l} - \epsilon_{\rm r})_{\rm cD},$$

$$\Delta A_{\rm trans} = \{[{\rm trans\ D}] - [{\rm trans\ L}]\}(\epsilon_{\rm l} - \epsilon_{\rm r})_{\rm tD},$$

$$J_{\rm cD} - J_{\rm cL} = I_0(1 - 10^{-A})\frac{(A_{\rm cD} - A_{\rm cL})}{A},$$

$$A_{\rm cD} - A_{\rm cL} = \epsilon_{\rm cD}[{\rm cis\ D}] - \epsilon_{\rm cL}[{\rm cis\ L}],$$

and similarly for the trans isomer. If LCP light is being used for the irradiation, then

$$\epsilon_{\rm cD} = \epsilon + \frac{(\epsilon_{\rm l} - \epsilon_{\rm r})_{\rm cD}}{2}$$

and

$$\epsilon_{\rm cL} = \epsilon - \frac{(\epsilon_{\rm l} - \epsilon_{\rm r})_{\rm cD}}{2}$$

therefore

$$A_{\rm cD} - A_{\rm cL} = \epsilon\{[{\rm cis\ D}] - [{\rm cis\ L}]\} + (C_0/2)(\epsilon_{\rm l} - \epsilon_{\rm r})_{\rm cD}$$

where

$$C_0 = [{\rm cis\ D}] + [{\rm cis\ L}]$$

If the wavelength of irradiation is the same as the wavelength for measurement of ΔA, and at the start of the irradiation of racemic cis complex, $[{\rm cis\ D}] - [{\rm cis\ L}] = 0$, the initial rates of change of ΔA in the cis and trans fractions are

$$\frac{{\rm d}(\Delta A_{\rm cis})}{{\rm d}t} =$$

$$-(2\phi_1 + \phi_2 + \phi_5)\frac{(C_0)}{2}(\epsilon_1 - \epsilon_{\rm r})_{\rm cD}{}^2 I_0 \frac{(1 - 10^{-A})}{A} \quad (8{\rm a})$$

$$\frac{{\rm d}(\Delta A_{\rm trans})}{{\rm d}t} =$$

$$(\phi_2 - \phi_5)\frac{(C_0)}{2}(\epsilon_1 - \epsilon_{\rm r})_{\rm cD}(\epsilon_1 - \epsilon_{\rm r})_{\rm tD} I_0 \frac{(1 - 10^{-A})}{A} \quad (8{\rm b})$$

By a similar route, the initial rates for an initially trans system are obtained as follows:

$$\frac{{\rm d}(\Delta A_{\rm cis})}{{\rm d}t} =$$

$$(\phi_3 - \phi_6)\frac{(C_0)}{2}(\epsilon_1 - \epsilon_{\rm r})_{\rm cD}(\epsilon_1 - \epsilon_{\rm r})_{\rm tD} I_0 \frac{(1 - 10^{-A})}{A} \quad (8{\rm c})$$

$$\frac{{\rm d}(\Delta A_{\rm trans})}{{\rm d}t} =$$

$$-(2\phi_4 + \phi_6 + \phi_3)\frac{(C_0)}{2}(\epsilon_1 - \epsilon_{\rm r})_{\rm tD}{}^2 I_0 \frac{(1 - 10^{-A})}{A} \quad (8{\rm d})$$

With these expressions, there are more than enough equations to solve for the six quantum yields. In fact, only eq 8a,b, and d were used since they yielded the highest precision. The resulting quantum yields are shown in Table III.

There has been an extensive amount of work done by others[9,15-24] on the thermal kinetics of geometrical and optical isomerization of tris chelates of metal ions with unsymmetrical ligands, with the purpose of establishing the mechanism of rearrangement. In general, the types of mechanism usually recognized as the possible ones are a twisting or a bond-rupture mechanism with either a square-pyramid or trigonal-bipyramid intermediate. Muetterties[25] has com-

Table III. Quantum Yields

Pathway	$10^3\phi$	Pathway	$10^3\phi$
1	$2.4 \pm 12\%$	4	$3.8 \pm 8\%$
2	$1.2 \pm 25\%$	5	$3.6 \pm 25\%$
3	$0.24 \pm 25\%$	6	$0.71 \pm 24\%$

pared the allowed pathways for a twisting mechanism with those for a bond-rupture with trigonal-bipyramid intermediate. A twisting mechanism would not allow pathways 2 and 3 in Figure 1, whereas the trigonal-bipyramid intermediate mechanism prohibits only pathway 1. On the other hand, a square-pyramid bond-rupture mechanism allows all pathways in Figure 1.[16] Thus the existence of values of quantum yields for pathways 2 and 3 in Table III indicates that both a bond-rupture mechanism and a twist mechanism are operative.

These results should be contrasted to those obtained by Kutal and Sievers for the thermal isomerization of $Cr(tfa)_3$ in the gas phase.[24] Although they observed only the isomerization, without any optical activity measurements, they concluded on the basis of activation parameters that the isomerization occurs through a twisting mechanism exclusively.

The ability of light to labilize chromium(III) complexes has been demonstrated many times,[26] but nearly all these studies have been in aqueous solutions, unlike the system studied here. Such photoreactivity is generally wavelength independent in the visible part of the spectrum and is attributed to the existence of metastable, reactive $^4T_{2g}$ or ^2E_g states (assuming O_h symmetry) to which the excited electronic states, $^4T_{1g}$ and $^4T_{2g}$, rapidly decay.[27] The results of the present study and the previous one involving $Cr(acac)_3$,[6] indicate that such a photolytically induced labilization can occur in nonaqueous solvent systems as well.

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Oxidation of Organic Compounds with Cerium(IV). XIX. Effect of Alkyl Substitution on the Oxidative Cleavage of Alkylphenylmethanols[1]
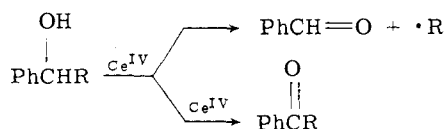
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Abstract: A series of alkylphenylmethanols was oxidized with ceric ammonium nitrate (CAN) in 50% aqueous acetonitrile at 80°. The benzaldehyde:alkyl phenyl ketone ratios determined from the product mixtures were used as measures of the relative rate constants for oxidative cleavage generating the respective alkyl radicals. The ratios found for the various alkyl groups are: ethyl, 4.13; 2-methylpropyl, 3.69; cyclopropylmethyl, 24.4; 5-hexenyl, 3.19; 4-methoxybutyl, 2.16; 3-methoxypropyl, 1.10; 2-methoxyethyl, 0.487; 4-bromobutyl, 0.58; 2-bromoethyl, 0.096; 2-chloroethyl, 0.48; 2-fluoroethyl, 0.22; cyclohexyl, 119; cyclopentyl, 66.1; cyclobutyl, 12.9. The CAN oxidation of ethyl(2-methoxyethyl)phenylmethanol generates 2-methoxyethyl and ethyl phenyl ketones by oxidative cleavage. The observed ratio of 2-methoxyethyl phenyl ketone:ethyl phenyl ketone is 7.73 which agrees very well with the value 8.48 calculated from the relative cleavage rate constants obtained from the secondary alcohols. This supports the assumption that the relative rate constants for ketone formation for the various secondary alcohols are approximately the same. From these results, it is concluded that the oxidative cleavage reaction of alkylphenylmethanols by CAN has a polar transition state which is influenced in a regular way by the inductive effect of the alkyl substituent. Substituents that withdraw electrons inductively, *e.g.*, methoxy groups and halogen atoms, retard oxidative cleavage. Neighboring groups which are known to greatly stabilize cations by hyperconjugation can accelerate oxidative cleavage. Neighboring groups which cause anchimeric assistance by lone pair participation, *e.g.*, methoxy groups and bromine atoms, do not enhance the oxidative cleavage reaction.

The oxidation of secondary alcohols by cerium(IV) generally gives products of oxidative cleavage in addition to ketone formation, and, in fact, often the major reaction is oxidative cleavage.[2] Oxidative cleavages of alcohols have been shown to be one-electron processes, and the transition state of the cerium(IV) reaction appears to be a polar one in which a fair amount of positive charge develops on the radical which is being formed.[2]

Recently we reported a study of the ceric ammonium nitrate (CAN) oxidation of a series of simple alkylphenylmethanols.[3] We assumed that the relative rate constants for oxidative cleavage to formation of the corresponding carbonyl compound were given by the ratios of benzaldehyde:alkyl phenyl ketone that were obtained from the alkylphenylmethanols.

We have extended this study to include alkylphenylmethanols that contain substituted alkyl groups or ones that possess structural features such as rings since relative rate constants for formation by metal ion oxidative cleavages of alcohols of only relatively simple radicals have been determined.[2c] The main features of this study are reported here.

Results

A series of alkylphenylmethanols was oxidized by 2 equiv of CAN in 50% aqueous acetonitrile at *ca.* 80°. Mixture of

CAN and the alcohols resulted in appearance of a red color attributed to complex formation. The red color faded to colorless or faint yellow within 1.5–20 min as the oxidations took place. The absolute yields of the recovered starting materials and products are reported in Table I. From the ratios of benzaldehyde:ketone that were obtained from the alkylphenylmethanols, it is seen that oxidative cleavage is the main pathway when the R group is a secondary alkyl group, but usually oxidative cleavage and ketone formation are both important when R is a primary alkyl group.[3] The material balance is good in all cases except for 2-chloroethylphenylmethanol where it is 129%. In this case, the workup resulted in an emulsion which probably caused some error in the determination of the absolute yields.

The difference between the benzaldehyde:ketone ratio found in this work for ethylphenylmethanol, 4.13, and that reported earlier,[3] 3.30, is small but real. The present value was determined more carefully and under slightly different conditions.

Cyclopropylphenylmethanol was found to be unstable to reaction conditions. In a control run using a cerium(III) solution (prepared from CAN and pinacol) and cyclopropylphenylmethanol, little starting material was found after work-up. The major product was isolated, and its nmr was found to be consistent with that of 4-phenylbut-3-en-1-ol. This product undoubtedly results from an acid-catalyzed rearrangement since aqueous CAN solutions are acidic.

(Cyclopropylmethyl)phenylmethanol when oxidized by CAN gives a benzaldehyde:ketone ratio that is significantly greater than those obtained from the other alcohols with