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## Oxidation of Organic Compounds with Cerium(IV). XIX. Effect of Alkyl Substitution on the Oxidative Cleavage of Alkylphenylmethanols<sup>1</sup>

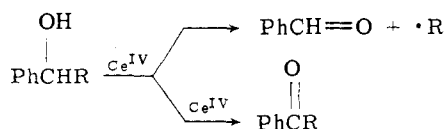
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**Abstract:** A series of alkylphenylmethanols was oxidized with ceric ammonium nitrate (CAN) in 50% aqueous acetonitrile at 80°. The benzaldehyde:alkyl phenyl ketone ratios determined from the product mixtures were used as measures of the relative 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.<sup>2</sup> 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.<sup>2</sup>

Recently we reported a study of the ceric ammonium nitrate (CAN) oxidation of a series of simple alkylphenylmethanols.<sup>3</sup> 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.<sup>2c</sup> 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.<sup>3</sup> The material balance is good in all cases except for 2-chloroethylphenylmethanol where it is 129%. In this case, the work-up 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,<sup>3</sup> 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

**Table I.** Absolute Yields of Recovered Starting Materials and Products from the CAN Oxidation of Alkylphenylmethanols, PhCHOHR<sup>a</sup>

R	Yield, %			Yield of PhCHO/ yield of PhCOR
	PhCHOHR	PhCOR	PhCHO	
Ethyl <sup>b</sup>	20.9 ± 0.3	14.8 ± 0.3	61.1 ± 0.7	4.13 ± 0.04
Isobutyl <sup>b</sup>	15.4 ± 1.6	15.1 ± 0.0	55.6 ± 0.0	3.69 ± 0.01
Cyclopropylmethyl	14.7 ± 0.4	3.15 ± 0.46	75.5 ± 1.4	24.4 ± 4.1
5-Hexenyl	36.5 ± 1.6	13.8 ± 0.4	44.0 ± 0.6	3.19 ± 0.13
4-Methoxybutyl	30.8 ± 0.6	21.8 ± 0.7	47.0 ± 0.7	2.16 ± 0.07
3-Methoxypropyl	45.5 ± 3.2	24.7 ± 1.7	26.9 ± 2.7	1.10 ± 0.18
2-Methoxyethyl	42.1 ± 1.7	39.8 ± 0.9	19.4 ± 0.4	0.487 ± 0.004
4-Bromobutyl <sup>b,c</sup>	26.0 ± 1.0	44.0 ± 0.0	25.0 ± 2.0	0.58 ± 0.04
2-Bromoethyl <sup>c</sup>	32.0 ± 10.0	62.0 ± 18.0	6.4 ± 1.5	0.096 ± 0.03
2-Chloroethyl <sup>b,c</sup>	61.0 ± 4.0	46.0 ± 4.0	22.0 ± 2.0	0.48 ± 0.06
2-Fluoroethyl <sup>c,d</sup>	47.0	45.0	10.0	0.22
Cyclohexyl	4.46 ± 0.62	0.753 ± 0.027	89.6 ± 0.9	119.0 ± 2.9
Cyclopentyl	23.4 ± 4.0	1.16 ± 0.26	74.4 ± 1.2	66.1 ± 14.8
Cyclobutyl	23.0 ± 4.1	4.79 ± 0.54	6.14 ± 3.9	12.9 ± 1.7

<sup>a</sup> In 50% aqueous acetonitrile at 80°; yields were determined by glpc using an internal standard and are based on at least three runs unless otherwise noted. <sup>b</sup> Results based on two runs; average instead of standard deviations are presented. <sup>c</sup> Yields were determined by nmr using an internal standard. <sup>d</sup> Results based on one run.

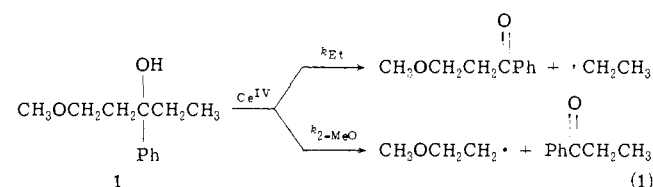
**Table II.** Absolute Yields of Recovered Starting Material and Products from the CAN Oxidation of Ethyl(2-methoxyethyl)phenylmethanol<sup>a</sup>

Compd	Yield, %
Ethyl(2-methoxyethyl)phenylmethanol	30.6 ± 0.6
Ethyl phenyl ketone	7.82 ± 0.35
2-Methoxyethyl phenyl ketone	60.3 ± 0.4
Yield of 2-methoxyethyl phenyl ketone yield of ethyl phenyl ketone	7.73 ± 0.39

<sup>a</sup> In 50% aqueous acetonitrile at 80°; yields were determined from three glpc runs.

primary alkyl groups. A mixture of allylphenylmethanol and (cyclopropylmethyl)phenylmethanol in the ratio of 1:1.12 was oxidized by 1 equiv of CAN. The ratio of the recovered starting materials was 1:1.19, respectively. These ratios were determined by glpc, and the nmr of the reaction mixture indicated a 20% yield of benzaldehyde. Thus the rate constants for oxidation of these two alcohols must be comparable.

The relative rate constants for ketone formation for all of the alkylphenylmethanols listed in Table I must be approximately the same if the benzaldehyde:ketone ratios for these alcohols can be used as a measure of their relative rate constants for oxidative cleavage. In order to partially establish the validity of this approximation, a tertiary dialkylphenylmethanol, ethyl(2-methoxyethyl)phenylmethanol (**1**), was oxidized with CAN (eq 1). The yields of products were de-



termined by glpc analysis using an internal standard and are reported in Table II. The oxidation was well behaved, and the material balance was high, 99%. The CAN oxidation of this tertiary alcohol resulted in two phenyl ketones since either the ethyl or 2-methoxyethyl group was cleaved off. If the relative rate constants for ketone formation for ethylphenylmethanol and 2-methoxyethylphenylmethanol are the same, the ratio of 2-methoxyethyl phenyl ketone:ethyl phenyl ketone obtained from CAN oxidation of **1** should be *ca.* 8.48 since

**Table III.** Effect of Temperature on the Benzaldehyde:Ketone Ratio<sup>a</sup>

Temp, °C	Reaction time, min	Material balance, %	Benzaldehyde/ketone
Ethylphenylmethanol			
80	10.5	96.7	4.13
50	138	93.5	2.87
30	1320	93	2.00
Cyclohexylphenylmethanol			
80	3.5	95	119
50	30	103	79.6
30	270	94	47.5

<sup>a</sup> Reaction with CAN in 50% aqueous acetonitrile; yields were determined by glpc using an internal standard.

$$\frac{[\text{CH}_3\text{OCH}_2\text{CH}_2\text{COPh}]}{[\text{CH}_3\text{CH}_2\text{COPh}]} = \frac{k_{\text{Et}}}{k_{2-\text{MeO}}} \approx \frac{k'_{\text{Et}}/k_{\text{ketone}}}{k'_{2-\text{MeO}}/k_{\text{ketone}}} = \frac{4.13}{0.487} = 8.48$$

where  $k_{\text{Et}}$  and  $k_{2-\text{MeO}}$  are defined in eq 1,  $k'_{\text{Et}}/k_{\text{ketone}}$  is the benzaldehyde:ketone ratio obtained from ethylphenylmethanol, and  $k'_{2-\text{MeO}}/k_{\text{ketone}}$  is the benzaldehyde:ketone ratio obtained from 2-methoxyethylphenylmethanol. The 2-methoxyethyl phenyl ketone:ethyl phenyl ketone ratio was found to be  $7.73 \pm 0.39$  which is in excellent agreement with the predicted value.

The mass spectrum of **1** also showed that in the gas phase the radical cation of **1** loses an ethyl radical in preference to a 2-methoxyethyl radical. At 70 eV, the ratio of the intensities of the peak at  $m/e$  165 ( $\text{P} - \text{C}_2\text{H}_5$ ) to that at  $m/e$  135 ( $\text{P} - \text{CH}_3\text{OC}_2\text{H}_4$ ) was 100/48, and, at 16 eV, this ratio was 100/24.

The effect of reaction temperature on the benzaldehyde:ketone ratio is presented in Table III. The effect is relatively small. A decrease in the reaction temperature of 50° decreases the benzaldehyde:ketone ratio by a factor of only 2 for ethylphenylmethanol and 2.5 for cyclohexylphenylmethanol. From these data,  $\Delta\Delta E_a$ 's for the competing reactions were calculated and are 3.0 and 4.0 kcal/mol for ethylphenylmethanol and cyclohexylphenylmethanol, respectively.

In general we have found that the radical produced in the cleavage reaction is oxidized to the corresponding alkyl nitrate or an olefin.<sup>3,4</sup> In this investigation, for most alcohols we did not study the products of the radical in detail, but the distinctive nitrate bands at 1660–1625 and at 1300–

1255  $\text{cm}^{-1}$  were observed in the ir spectra of the product mixtures from the CAN oxidation of many of the alkylphenylmethanols. The fate of the radical was studied in greater detail for the oxidative cleavage of cyclopentylphenylmethanol and cyclohexylphenylmethanol. From the cyclopentyl compound, 40% cyclopentene and 43% cyclopentyl nitrate were obtained.<sup>5</sup> From the cyclohexyl compound, 37% cyclohexene, 40% cyclohexyl nitrate, 15–20% *N*-cyclohexylacetamide, and 1–5% cyclohexanol were obtained. Acetamides have been observed before<sup>3</sup> and presumably arise from attack of the cation by acetonitrile.

Cyclohexylphenylmethanol was oxidized by CAN under a variety of conditions to determine what factors might influence the distribution of olefin and nitrate products. With temperatures of 120 (sealed tube experiment), 80, and 30°, no significant change in the distribution was found. Little effect on this distribution was found when the reaction solvent was changed from 20 to 50 to 90% aqueous acetonitrile.

## Discussion

That the relative rate constants for ketone formation for alkylphenylmethanols are approximately the same is indicated by the results obtained from the CAN oxidation of the tertiary alcohol ethyl(2-methoxyethyl)phenylmethanol (1), and thus the benzaldehyde:ketone ratio for these alkylphenylmethanols can be used as a measure of their relative rate constants for oxidative cleavage.

The benzaldehyde:ketone ratios for ethylphenylmethanol and cyclohexylphenylmethanol at several temperatures are presented in Table III. From these values, the ratio of the rate constant for formation of the cyclohexyl radical to that for the ethyl radical is 28.8 at 80°, 27.7 at 50°, and 23.8 at 30°. Thus a temperature change of 50° has only a small effect on these ratios. It is interesting to note that the relative rate constant for ejection of the cyclohexyl radical vs. the ethyl radical from *tert*-alkoxy radicals is reported as 23 at 80°.<sup>6</sup>

The effect of ring size upon the rate constants for formation of cyclic radicals varies with the mode of radical generation.<sup>7,8</sup> Thermolysis of various cycloalkyl azo compounds always shows larger rate constants for the five-membered ring than the six-membered ring. Decomposition of azo-1-methylcyclopentane is *ca.* ten times faster than that of azo-1-methylcyclohexane.<sup>7</sup> In contrast, the rate constants for homolytic fragmentation of cycloalkyl peroxy esters decrease roughly as the size of the ring decreases and do not pass through a minimum for the six-membered ring as observed for thermolysis of azo compounds or for carbenium ion formation.<sup>7,8</sup> Röchardt's interpretation is that ring strain effects have no appreciable influence on the decomposition of peroxy esters and that the C-CO bond is only weakly stretched in the transition state, and the alkyl carbon atom has essentially tetrahedral geometry.<sup>7,8</sup> He points out that polar effects are less important in the thermolysis of symmetrical azo alkanes than for the fragmentation of peroxy esters. He concludes that polar effects are important for radical formation reactions in which the transition state occurs early on the reaction coordinate as with fragmentation of peroxy esters.<sup>8</sup>

Thus the relative rates of reactivity of the five- and six-membered ring compounds should be very informative in determining the position of the transition state and the relative importance of polar effects for any reaction in question. A polar effect has been observed for the metal ion oxidative cleavage of alcohols,<sup>2</sup> and so this reaction is expected to form the cyclohexyl radical faster than the cyclopentyl radi-

cal. This is the order that was found as indicated by the relative rate constants for oxidative cleavage from the benzaldehyde:ketone ratios presented in Table I for the cyclobutyl, cyclopentyl, and cyclohexyl systems which are 1.0, 5.1, and 9.2, respectively. The relative rate constants for decomposition of the corresponding cyclic diacyl peroxides are 1.0, 4.3, and 8.3,<sup>9</sup> which agree very well with our data. A direct comparison of the rate of formation of the cyclohexyl vs. the cyclopentyl radical reveals excellent agreement among reactions influenced by polar effects. This ratio is 2.56 for the internal competition during decomposition of 1-cyclopentyl-1-cyclohexyl ethyl hypochlorite,<sup>7</sup> 2.56 for comparison of the relative rates of cyclohexyl vs. ethyl and cyclopentyl vs. ethyl ejection from *tert*-alkoxy radicals,<sup>6</sup> 1.9 for diacyl peroxide decomposition,<sup>9</sup> and 1.8 for the CAN oxidative cleavage of alcohols reported here. From these comparisons, it is clear that the transition state of the oxidative cleavage reaction of an alkylphenylmethanol with CAN lies early on the reaction coordinate and is polar.

For the CAN oxidation of several alkylphenylmethanols that produce primary alkyl radicals, we have found that the benzaldehyde:ketone ratios are *ca.* 4. The benzaldehyde:ketone ratios for ethyl-, 2-methylpropyl-, 3,3-dimethylbutyl-,<sup>10</sup> and 5-hexenylphenylmethanols are 4.13, 3.69, 3.27, and 3.19, respectively. These results indicate that the size of the primary radical which is being formed during the oxidative cleavage does not significantly affect its rate of formation. A similar conclusion can be drawn for the fragmentation of alkoxy radicals.<sup>11,12</sup>

The 5-hexenyl radical, which can undergo cyclization to a five-membered ring, has been studied intensively.<sup>13–15</sup> Study of the kinetics and products of the thermal decomposition of 6-heptenyl peroxide, which produces the 5-hexenyl radical, indicates that initial cleavage occurs without a neighboring group effect from the double bond.<sup>13</sup> Study of the reaction of 6-bromo-1-hexene with tributylstannane also yields no evidence for participation of the double bond during radical generation.<sup>14</sup> Our results with CAN oxidation of 5-hexenylphenylmethanol also indicate no participation of the double bond during oxidative cleavage.

The polar nature of the transition state for the CAN oxidative cleavage of alcohols suggests that electron-withdrawing substituents on the alkyl group of an alkylphenylmethanol should retard its rate of oxidation. The benzaldehyde:ketone ratios obtained from the CAN oxidation of a series of methoxy-substituted alkylphenylmethanols, shown in Table I, indicate that the methoxy substituents significantly retard the cleavage reaction. From these data, it is seen that the relative rate constant for oxidative cleavage of even the 4-methoxybutyl alcohol is slower than that of ethylphenylmethanol, and the relative rate constants for oxidative cleavage decrease regularly from the 4-methoxybutyl to the 2-methoxyethyl alcohol. Methoxymethylphenylmethanol is a monomethyl ether of a 1,2-glycol and so is expected<sup>16</sup> and was found<sup>17</sup> to undergo oxidative cleavage exclusively.

The effect of methoxy groups on the relative rate constants for oxidative cleavage is most readily explained by their inductive effect. The stability of the polar transition state for the cleavage reaction must be decreased by the electron-withdrawing methoxy groups.

Any direct interaction of the methoxy groups is unlikely since the formation constants for the 1:1 cerium(IV)-alcohol complexes for hexanol, 2-methoxyethanol, and 3-ethoxypropanol are very similar.<sup>18</sup> Moreover the good material balance from the oxidation of the methoxy alcohols rules out any attack at the methoxy group which leads to products other than those expected from attack at the hydroxy group.

Although 2- and 3-methoxy groups retard the rates of solvolysis of  $\omega$ -methoxy-1-alkyl *p*-bromobenzenesulfonates, the 4-methoxy group leads to a rate increase.<sup>19</sup> This rate increase is ascribed to neighboring group participation which involves the formation of a five-membered ring. In the CAN oxidative cleavage reaction, the low rate constant for cleavage for the 4-methoxy alcohol indicates that neighboring group participation by the methoxy groups is unimportant.

A halogen substituent on the alkyl radical which is being formed during the oxidative cleavage also significantly retards the cleavage. In Table I, the benzaldehyde:ketone ratios from the CAN oxidation of several halogen substituted alkylphenylmethanols show this retardation. Even if the halogen is four methylene groups removed from the radical center, as it is in the case of the 4-bromobutyl alcohol, there is a marked reduction in cleavage vs. ketone formation. In fact, for all of the halogen compounds studied, oxidative cleavage is the minor reaction in favor of formation of ketone.

As with the methoxy groups, the relative rate constants for oxidative cleavage of the haloalkyl alcohols are readily accounted for by the inductive effect. However, the observed order of cleavage for the 2-bromoethyl, 2-chloroethyl, and the 2-fluoroethyl is not explained by the inductive effect, and it is possible that some direct interaction of the halogens and CAN exists since the formation constants for the 1:1 cerium(IV)-alcohol complexes for ethanol and 2-chloroethanol are respectively  $0.74 \pm 0.05$  and  $0.13 \pm 0.2$ .<sup>18</sup> Quantitative measures of the inductive effect of substituents show that the inductive effects of the three halogens should be about the same.<sup>20,21</sup>

The halogens are reported<sup>20,21</sup> to be more electron withdrawing than the methoxy group which in turn is reported to be more electron withdrawing than a carbon-carbon double bond. This order is nicely manifested by the relative rate constants for formation of the respective 4-substituted butyl radicals presented in Table I.

Recently there has been a great deal of interest in the possibility of the existence and effects of bridged halogen radicals.<sup>22</sup> Although there is evidence that a  $\beta$ -bromoalkyl free radical is bridged,<sup>22</sup> our results from the CAN oxidation of 2-bromoethylphenylmethanol show no evidence for participation by the  $\beta$ -bromine atom during oxidative cleavage. The simplest way to interpret the low benzaldehyde:ketone ratio is that the transition state is relatively destabilized by the inductive effect of the bromine.

The radical produced from the oxidative cleavage of 2-bromoethylphenylmethanol, the 2-bromoethyl radical, has been reported to fragment very rapidly to ethylene and a bromine atom even at low temperature.<sup>23</sup> We could not detect the products of the 2-bromoethyl radical in our study since the oxidative cleavage was such a minor reaction.

The polar nature of the transition state of the CAN oxidative cleavage of alcohols also suggests that neighboring groups which stabilize cations may accelerate the corresponding oxidative cleavages. The ratio of cleavage vs. ketone formation for the CAN oxidation of cyclopropylmethylphenylmethanol is 24.4, whereas the corresponding ratio for the model compound, isobutylphenylmethanol, is 3.69 which is very close to the ratio of 4.13 obtained for ethylphenylmethanol. It is clear that cleavage leading to the cyclopropylmethyl radical is more rapid than that leading to a normal primary carbon radical. The rate constants for formation of the cyclopropylmethyl radical relative to the rate constants for formation of normal primary carbon radicals have been found to be 3.3–55 for a number of different methods of generating free radicals.<sup>24</sup> These rate enhance-

ments for the formation of cyclopropylmethyl radicals, including the one reported here for the CAN oxidative cleavage reaction, are most likely due to stabilization of the radical by the cyclopropane ring by hyperconjugation or vertical stabilization,<sup>25</sup> not bridging in the usual sense.

In conclusion, the benzaldehyde:ketone ratios obtained from the CAN oxidation of alkylphenylmethanols appear to be good measures of the relative rate constants for oxidative cleavage. The transition state is polar and influenced in a regular way by the inductive effect of the alkyl substituent. Neighboring groups which are known to greatly stabilize cations by hyperconjugation (vertical stabilization) can accelerate oxidative cleavage. Neighboring groups which cause anchimeric assistance by bridging, *i.e.*, Br and CH<sub>3</sub>O, do not enhance the oxidative cleavage reaction.

## Experimental Section

**Methods and Materials.** Most equipment and methods have been previously described.<sup>1a</sup> High resolution mass spectra were recorded with an Associated Electronics Industries MS-902 instrument. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich., unless indicated otherwise. Cyclopropyl, cyclohexyl, ethyl, and 2-chloroethyl phenyl ketones, cyclopropylphenylmethanol, cyclopentanol, chloromethyl methyl ether, ethyl benzoylacetate, and 1,3-dibromopropane were obtained from Aldrich Chemical Co. Cyclopentyl and cyclobutyl phenyl ketones were obtained from Peninsular ChemResearch. Isobutyl phenyl ketone was obtained from Eastman Kodak Co. 2-Bromoethyl phenyl ketone was obtained from Frinton Laboratories. 1,1,2,2-Tetrachloroethane was obtained from Mallinckrodt Chemical Works. 5-Hexenol was obtained from Columbia Organic Chemicals. All compounds were used without further purification except 2-bromoethyl phenyl ketone which was recrystallized from pentane.

The following columns were used for glpc analysis: column A, 1 m  $\times$  6.35 mm aluminum column, 20% Carbowax 20M on Chromosorb W; column B, 0.5 m  $\times$  6.36 mm aluminum column, 20% Carbowax 20M on Chromosorb W; column C, 1 m  $\times$  6.35 mm aluminum column, 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on Chromosorb P; column D, 1.2 m  $\times$  6.36 mm aluminum column, 20% TCEP on Chromosorb P; column E, 1 m  $\times$  6.35 mm aluminum column, 20% SE 30 on Chromosorb W.

**Ethylphenylmethanol.** Commercial ethylphenylmethanol (Aldrich) was found to contain about 6% of the corresponding ketone as an impurity based on glpc analysis. This commercial material was treated with sodium borohydride in aqueous ethanol, and the recovered ethylphenylmethanol was found to be free of ketone by glpc and nmr analysis.

**Isobutylphenylmethanol.** Isobutyl phenyl ketone was reduced with sodium borohydride in 95% ethanol: bp 114° (9 mm) [lit.<sup>26</sup> bp 98° (4 mm)]; nmr (CCl<sub>4</sub>)  $\delta$  7.03 (s, 5), 4.40 (m, 1), 3.63 (d, 1, *J* = 3.5 Hz), 1.4 (m, 3), and 0.84 (d, 6, *J* = 6.0 Hz).

**Allylphenylmethanol** was prepared from the Grignard reagent of allyl bromide and benzaldehyde: bp 108° (11 mm) [lit.<sup>27</sup> bp 106–108° (10 mm)]; nmr (CCl<sub>4</sub>)  $\delta$  7.03 (s, 5), 5.50 (m, 1), 4.84 (m, 2), 4.37 (t, 1, *J* = 6.5 Hz), 3.55 (s, 1), and 2.26 (t, 2, *J* = 6.5 Hz).

**(Cyclopropylmethyl)phenylmethanol** was prepared according to the procedure of Lansbury and Pattison<sup>27</sup> which was modified by using the zinc-copper couple described by Rawson and Harrison:<sup>28</sup> bp 109–111° (5.5 mm) [lit.<sup>27</sup> bp 125–130° (12 mm)]; nmr (CCl<sub>4</sub>)  $\delta$  7.16 (s, 5), 4.49 (t, 1, *J* = 6.5 Hz), 3.75 (s, 1), 1.44 (m, 2), 0.32 (m, 3), and -0.02 (m, 2).

**Cyclopropylmethyl phenyl ketone** was prepared from the corresponding alcohol using Collins reagent.<sup>29</sup> The crude product was purified by chromatography on a silica gel column using hexane as the eluent: nmr (CCl<sub>4</sub>)  $\delta$  7.85–7.60 (m, 2), 7.4–7.2 (m, 3), 2.65 (d, 2, *J* = 7.0 Hz), and 1.5–0.0 (m, 5); ir (CCl<sub>4</sub>) 3080 (w), 1696 (s), 1211 (m), and 1020 (m) cm<sup>-1</sup>; mol wt (mass spec) 160.0889 (calcd for C<sub>11</sub>H<sub>12</sub>O, 160.0888).

**5-Hexenylphenylmethanol.** 6-Bromohexene was prepared from 5-hexenol using bromine and triphenylphosphine instead of triphenyl phosphite as described previously.<sup>30</sup> 5-Hexenylphenylmethanol was prepared from the Grignard reagent of 6-bromohex-

ene and benzaldehyde. The crude product was distilled [bp 114–116° (2 mm)] to give a colorless oil that contained a small amount of the corresponding ketone. An additional distillation did not remove the ketone so the material was treated with sodium borohydride in ethanol. After work-up, a colorless oil was obtained which was free of any carbonyl compounds: nmr (CCl<sub>4</sub>)  $\delta$  7.16 (s, 5), 6.1–4.7 (overlapping multiplets, 3, vinyl), 4.4 (m, 1), 4.0 (s, 1, OH), and 2.1–1.05 (overlapping multiplets, 8); ir (CCl<sub>4</sub>) 3620 (m), 2940 (s), 2860 (s), 1650 (m), 1500 (m), and 1460 (s) cm<sup>-1</sup>.

*Anal.* Calcd for C<sub>13</sub>H<sub>18</sub>O: C, 82.06; H, 9.53. Found: C, 82.00; H, 9.42.

**5-Hexenyl phenyl ketone** was prepared by a Jones oxidation of the alcohol as described by Meinwald and coworkers:<sup>31</sup> nmr (CCl<sub>4</sub>)  $\delta$  8.0–7.7 (m, 2), 7.5–7.2 (m, 3), 6.0–4.8 (m, 3, vinyl), 2.85 (t, 2, *J* = 7.0 Hz), and 2.2–1.2 (overlapping multiplets, 6); ir (CCl<sub>4</sub>) 2950 (s), 1700 (s), 1600 (m), and 1450 (m) cm<sup>-1</sup>; mass spectrum (70 eV) *m/e* 188 (P), 120, 105, 83, 82, and 77; mol wt (mass spec) 188.1201 (calcd for C<sub>13</sub>H<sub>16</sub>O, 188.1201).

**4-Methoxybutylphenylmethanol** was prepared from the Grignard reagent of 4-methoxybutyl bromide<sup>32</sup> and benzaldehyde. The crude product contained a small amount of the alkyl phenyl ketone as an impurity which was not removed by distillation. The product was treated with sodium borohydride, and the recovered material was free of ketone: bp 119–122° (2 mm) [lit.<sup>33</sup> bp 122° (2 mm)]; nmr (CCl<sub>4</sub>)  $\delta$  7.16 (s, 5), 4.4 (m, 1), 3.5 (s, 1, OH), 3.3–3.1 (overlapping signals, 5, s, at 3.12, OCH<sub>3</sub>), and 1.8–1.0 (m, 6); ir (neat) 3450 (broad peak), 2950, 2880, 1460, and 1125 cm<sup>-1</sup>.

**4-Methoxybutyl phenyl ketone**<sup>34</sup> was prepared by a Jones oxidation of the alcohol:<sup>31</sup> nmr (CCl<sub>4</sub>)  $\delta$  8.0–7.75 (m, 2), 7.5–7.2 (m, 3), 3.45–3.15 (overlapping signals, 5, s at 3.21, OCH<sub>3</sub>), 2.88 (m, 2), and 2.0–1.2 (m, 4); ir (neat) 2950, 2880, 1695, 1455, and 1125 cm<sup>-1</sup>.

**3-Methoxypropyl Phenyl Ketone.** To 10 g (0.0685 mol) of cyclopropyl phenyl ketone dissolved in 50 ml of absolute methanol was added 3 ml of concentrated sulfuric acid. The mixture was heated to reflux for 9 days and then poured into 100 ml of ether and 300 ml of water. The ether layer was separated, and the aqueous phase was extracted two times with 100 ml of ether. The organic portions were combined and washed with 100 ml of 1 *M* aqueous sodium bicarbonate. The organic liquid was dried (MgSO<sub>4</sub>), filtered, and concentrated to give 10.7 g of a yellow oil which was distilled to give a colorless oil, 7.6 g, 66% yield: bp 136° (10 mm) [lit.<sup>35</sup> bp 103–104° (1 mm)]; nmr (CCl<sub>4</sub>)  $\delta$  7.9 (m, 2), 7.4 (m, 3), 3.38 (t, 2, *J* = 6.0 Hz), 3.25 (s, 3), 2.98 (t, 2, *J* = 7.0 Hz), and 1.92 (overlapping triplets, 2, *J* = 6.0, 7.0 Hz); ir (CCl<sub>4</sub>) 2930 (m), 2875 (m), 1690 (s), 1555 (m), 1450 (m), 1215 (m), 1121 (s), 1000 (m), and 830 (s) cm<sup>-1</sup>; mass spectrum (80 eV) *m/e* (rel intensity) 178 (P), 163, 146, 133, 121 (88), 120 (100), 106 (83), 105 (100), 77 (100), 59 (90), and 45 (95).

*Anal.* Calcd for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>: C, 74.13; H, 7.92; mol wt 178.0994. Found:<sup>36</sup> C, 73.78; H, 7.80; mol wt (mass spec) 178.0996.

**3-Methoxypropylphenylmethanol** was prepared by the sodium borohydride reduction of the ketone: bp 121–122° (5 mm); nmr (CCl<sub>4</sub>)  $\delta$  7.18 (s, 5), 4.44 (m, 1), 3.68 (s, 1, OH), 3.20 (t, 2, *J* = 6.0 Hz), 3.14 (s, 3), and 1.7–1.3 (overlapping multiplets, 4); ir (CCl<sub>4</sub>) 3620 (m), 3430 (m), 2930 (s), 2875 (s), 1452 (m), and 1121 (s) cm<sup>-1</sup>; mass spectrum (16 eV) *m/e* (rel intensity) 180 (2.6, P), 179 (16), 162 (6.3), 148 (12.5), 120 (31), 117 (25), 107 (100), 105 (32), 91 (13.5), 79 (43), and 77 (31).

*Anal.* Calcd for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>: C, 73.30; H, 8.95. Found: C, 73.17; H, 8.95.

**2-Methoxyethylphenylmethanol.** 3-Methoxy-1-phenylpropyl chloride was prepared by treating chloromethyl methyl ether and styrene with anhydrous zinc chloride<sup>37a</sup> in carbon tetrachloride:<sup>37b</sup> nmr (CCl<sub>4</sub>)  $\delta$  7.25 (m, 5), 5.04 (t, 1, *J* = 7.5 Hz), 3.6–3.0 (m, 2), 3.20 (s, 3), and 2.16 (m, 2). The chloride was converted to the alcohol with 20% aqueous potassium hydroxide:<sup>38</sup> bp 111–115° (5 mm) [lit.<sup>38</sup> bp 112–113° (5 mm)]; nmr (CCl<sub>4</sub>)  $\delta$  7.18 (s, 5), 4.64 (t, 1, *J* = 6.5 Hz), 3.8 (s, 1, OH), 3.28 (m, 2), 3.12 (s, 3), and 1.77 (m, 2); ir (CCl<sub>4</sub>) 3615 (m), 3520 (s), 2920 (m), 1460 (m), 1390 (m), and 1123 (m) cm<sup>-1</sup>.

**2-Methoxyethyl phenyl ketone** was prepared by a Jones oxidation<sup>31</sup> of the alcohol: bp 121–123° (10 mm) [lit.<sup>39</sup> bp 125–126° (16 mm)]; nmr (CCl<sub>4</sub>)  $\delta$  7.8 (m, 2), 7.3 (m, 3), 3.64 (t, 2, *J* = 6.2 Hz), 3.24 (s, 3), and 3.04 (t, 2, *J* = 6.2 Hz); ir (CCl<sub>4</sub>) 2930 (m),

2900 (m), 1695 (s), 1460 (m), 1230 (m), 1190 (m), and 1128 (s) cm<sup>-1</sup>.

**Ethyl(2-methoxyethyl)phenylmethanol** was prepared from the Grignard reagent of ethyl bromide and 2-methoxyethyl phenyl ketone: bp 117–118° (9 mm); nmr (CCl<sub>4</sub>)  $\delta$  7.25 (m, 5), 3.65 (s, 1), 3.5–3.1 (overlapping signals, 5, s at 3.12 is OCH<sub>3</sub>), 2.2–1.5 (overlapping signals, 4, q at 1.85, *J* = 7.0 Hz), and 0.7 (t, 3, *J* = 7.0 Hz); ir (CCl<sub>4</sub>) 3510 (s), 2930 (s), 1440 (m), 1580 (m), and 1110 (s) cm<sup>-1</sup>; mass spectrum (70 eV) *m/e* (rel intensity) 176 (10.5), 165 (100), 135 (47.5), 133 (58), 105 (79), and 77 (29).

*Anal.*<sup>36</sup> Calcd for C<sub>12</sub>H<sub>18</sub>O<sub>2</sub>: C, 74.19; H, 9.34. Found: C, 73.83; H, 9.25.

**4-Bromobutyl phenyl ketone** was prepared according to the procedure of Bieber and Eisman.<sup>40</sup> The product was recrystallized from pentane: mp 57.5–58.0° (lit.<sup>40</sup> mp 52–54°, lit.<sup>41</sup> mp 61°); nmr (CCl<sub>4</sub>)  $\delta$  7.8 (m, 2), 7.4 (m, 3), 3.4 (m, 2), 2.9 (m, 2), and 1.9 (m, 4); ir (CCl<sub>4</sub>) 1704 (s), 1608, 1458, and 1228 cm<sup>-1</sup>.

**4-Bromobutylphenylmethanol** was prepared by the sodium borohydride reduction of the ketone. This material was distilled and then recrystallized from pentane: bp 129° (1 mm); nmr (CCl<sub>4</sub>)  $\delta$  7.28 (s, 5), 4.49 (t, 1, *J* = 5.8 Hz), 3.28 (t, 2, *J* = 6.0 Hz), 3.26 (s, 1, OH), and 2.0–1.0 (overlapping signals, 6); ir (CCl<sub>4</sub>) 3622, 2945, 1461, and 1060 cm<sup>-1</sup>; mass spectrum (70 eV) *m/e* 244, 242, 226, 224, 162 (base), 107, 105, 91, and 77; mol wt (mass spec) 242.0302 (calcd for C<sub>11</sub>H<sub>15</sub>BrO, 242.0307).

**2-Bromoethylphenylmethanol** was prepared by the sodium borohydride reduction at low temperature:<sup>42</sup> bp 115–117° (2 mm); nmr (CCl<sub>4</sub>)  $\delta$  7.12 (s, 5), 4.61 (t, 1, *J* = 8.0 Hz), 3.4–3.1 (m, 3), and 2.2–1.8 (m, 2) [lit.<sup>43</sup> bp 98° (1 mm); nmr  $\delta$  7.2 (s, 5), 4.7 (t, 1, *J* = 5 Hz), 3.5–3.15 (m, 2), and 2.2–1.9 (m, 2)].

**2-Chloroethylphenylmethanol** was prepared by the sodium borohydride reduction at low temperature:<sup>42</sup> bp 125–130° (6–8 mm) [lit.<sup>44</sup> 130–132° (8 mm)]; nmr (CCl<sub>4</sub>)  $\delta$  7.10 (s, 5), 4.62 (m, 1), 3.6–3.0 (m, 3), and 2.1–1.7 (m, 2).

**2-Fluoroethylphenylmethanol** was synthesized from 2-chloroethylphenylmethanol, potassium fluoride, and potassium hydrogen fluoride in glycerol:<sup>45</sup> bp 121–122° (12 mm) [lit.<sup>45</sup> bp 96° (4 mm)]; nmr (CCl<sub>4</sub>)  $\delta$  7.24 (s, 5), 5.0–4.5 (m, 2), 4.2–3.9 (m, 1), 2.3–2.0 (m, 1), and 1.9–1.7 (m, 2); ir (CCl<sub>4</sub>) 3620, 2960, 1550, 1250, and 1030 cm<sup>-1</sup>; mass spectrum (70 eV) *m/e* 154, 135, 107, 105, 91, 79, and 77.

**Cyclohexylphenylmethanol** was prepared by the sodium borohydride reduction of the ketone. The product was distilled and the colorless oil obtained crystallized after standing for 3 days: bp 106° (1 mm); mp 49–50° (lit.<sup>46</sup> mp 49–50°); nmr (CCl<sub>4</sub>)  $\delta$  7.15 (s, 5), 4.12 (d, 1, *J* = 6.0 Hz), 3.1 (s, 1), and 2.0–0.8 (overlapping signals, 11).

**Cyclopentylphenylmethanol** was prepared by the sodium borohydride reduction of the ketone: bp 119° (2 mm) [lit.<sup>47</sup> bp 142–143.5° (13 mm)]; nmr (CCl<sub>4</sub>)  $\delta$  7.12 (s, 5), 4.12 (d, 1, *J* = 7.5 Hz), 3.05 (s, 1), and 2.2–0.8 (overlapping signals, 9).

**Cyclopentene** was prepared from cyclopentanol and sulfuric acid, bp 42–43° (lit.<sup>48</sup> bp 45–46°).

**Cyclopentyl nitrate** was prepared from cyclopentyl alcohol and a mixture of concentrated nitric and sulfuric acids according to the procedure of Kornblum and Teitelbaum:<sup>49</sup> bp 86° (60 mm) [lit.<sup>49</sup> bp 74° (30 mm)]; nmr (CCl<sub>4</sub>)  $\delta$  5.3 (m, 1) and 1.8 (m, 8).

**Cyclohexyl nitrate** was prepared from cyclohexyl alcohol and a mixture of concentrated nitric acid and concentrated sulfuric acid by a procedure<sup>50</sup> which appeared to be much more dangerous than that of Kornblum and Teitelbaum:<sup>49</sup> bp 45° (4 mm); ir (CCl<sub>4</sub>) 2940 (m), 1630 (vs), 1455 (w), 1280 (vs), 1011 (w), 947 (w), 902 (w), 870 (s), and 845 (w) cm<sup>-1</sup> [lit.<sup>51</sup> bp 70° (4 mm); ir 1626 (vs), 1464 (m), 1280 (vs), 1007 (m), 942 (m), 902 (m), 870 (vs), and 843 (m) cm<sup>-1</sup>].

**Cyclobutylphenylmethanol** was prepared by the sodium borohydride reduction of the ketone: bp 97° (1 mm) [lit.<sup>27</sup> bp 121–122° (5 mm)]; nmr (CCl<sub>4</sub>)  $\delta$  7.10 (s, 5), 4.25 (d, 1, *J* = 7.5 Hz), 3.78 (s, 1), 2.35 (m, 1), and 1.71 (m, 6).

**CAN Oxidations.** The alkylphenylmethanols were oxidized by 2 equiv of CAN in 50 or 56% aqueous acetonitrile. Absolute yields of starting material and products were determined by glpc or nmr analysis using internal standards. Products were determined by glpc peak enhancement or collection and spectral analysis. Methyl benzoate was used as the internal standard for glpc analysis for the

Table IV. Oxidation Procedure and Analysis for the Various Alcohols

Alcohol	Pro-cedure	Reac-tion time, min	Glpc column	Glpc column temp, °C	Glpc temp program
2-Methylpropylphenylmethanol	B	19	A	95	1°/min (to 165°)
(Cyclopropylmethyl)phenylmethanol	B	4	C	75	1°/min (to 165°)
5-Hexenylphenylmethanol	B	12	A	145	(Temp increased to 212° after elution of standard)
	(1/8 scale)				
4-Methoxybutylphenylmethanol	A	11	A	130	(Temp increased to 210° after elution of standard)
3-Methoxypropylphenylmethanol	A	10	A	130	(Temp increased to 220° after elution of standard)
2-Methoxyethylphenylmethanol	A	9	B	100	(Temp increased to 165° after elution of standard)
Cyclohexylphenylmethanol	A	3.5	A	130	(Temp increased to 205° after elution of standard)
Cyclopentylphenylmethanol <sup>a</sup>	B	2	D	95	(Temp increased to 160° after elution of standard)
Cyclobutylphenylmethanol	B	4	D	80	1°/min (to 150°)
4-Bromobutylphenylmethanol <sup>b</sup>	A	9			
2-Bromoethylphenylmethanol <sup>b</sup>	A	8			
2-Chloroethylphenylmethanol <sup>b</sup>	A	20			
2-Fluoroethylphenylmethanol <sup>b</sup>	A	8			
Ethyl(2-methoxyethyl)phenylmethanol	A	8.5	E	135	

<sup>a</sup> Yields of cyclopentyl nitrate and cyclopentene relative to benzaldehyde were determined by nmr using the signals at  $\delta$  5.3, 5.65, and 9.95, respectively. <sup>b</sup> The ether was removed by distillation and the sample analyzed by nmr.

oxidation mixtures from the alkylphenylmethanols. The glpc scans were photocopied, and the copies were cut and weighed. Yields determined relative to standard were corrected by factors obtained from control experiments. For the glpc analysis of the oxidation of **1**, cyclopentyl phenyl ketone was used as the internal standard.

For nmr analysis 1,1,2,2-tetrachloroethane was used as an internal standard. The aldehyde proton of benzaldehyde was compared directly with the standard. Other yields were determined by comparison of the total aromatic region and the ortho protons with standard. The typical oxidation mixture had a characteristic nmr:  $\delta$  9.95 (s, CHO), 8.1–7.7 (m, ortho H), 7.6–7.4 (m, meta and para H), ~7.2 (s, 5 H), 6.0 (s, standard). Since the yield of benzaldehyde was determined by direct comparison with standard, the yields of the ketone and alcohol could be determined by simple calculations.

Correction factors were determined in every case with the exception of the 2-fluoro alcohol and were found to be quite similar. The usual control experiment consisted of the preparation of a pseudo-reaction mixture. Typically 1 equiv each of alcohol, ketone, and benzaldehyde and 2 equiv of Ce(III) (prepared *in situ* from CAN reduced with pinacol) were mixed together and subjected to the same reaction conditions, work-up, and analysis as the actual oxidation mixtures. In this way, correction factors were determined, and the stability of the products to the reaction conditions was ascertained.

The specific conditions and methods of analysis for each alcohol are as follows.

**Ethylphenylmethanol. Procedure A.** Into a 10-ml round-bottom flask containing a stirring bar was placed 2 ml of acetonitrile, 1 ml of water, and 1 ml of a 1 M solution of ethylphenylmethanol in acetonitrile. Then 2 ml of 1 M aqueous CAN was added resulting in 0.167 M alcohol and 0.33 M CAN. The flask was fitted with a condenser and placed in an oil bath at 80–85°, and stirring of the 56% aqueous acetonitrile solution was started. After 10.5 min, the red color had faded to colorless, and the heating was stopped. After the mixture had cooled to room temperature, 0.5 ml of a 1 M solution of methyl benzoate in acetonitrile was added. About 3 ml of saturated aqueous sodium chloride solution was added, and the mixture was extracted twice with 3 ml of ether. The combined extracts were washed with 3 ml of saturated sodium chloride, twice with 3 ml of 1 M aqueous sodium bicarbonate, and once with 3 ml of saturated aqueous sodium chloride. It was dried (MgSO<sub>4</sub>), filtered, and analyzed on column A at 130°, 60 ml/min, and temperature programming 1°/min.

**Procedure B.** This was essentially the same as that previously outlined,<sup>3</sup> except that an 80–85° oil bath was used as the heat source instead of a steam bath. The reaction took 15 min. The solution was 50% aqueous acetonitrile, 0.25 M alcohol, and 0.5 M CAN.

Procedure A was used for two runs in a 50° oil bath and two runs in a 30° oil bath.

**Cyclohexylphenylmethanol.** See Table IV. Cyclohexylacetamide was collected by glpc from reaction mixtures and recrystallized from hexane: mp 104–105° (lit.<sup>52</sup> mp 103–104°); nmr (CCl<sub>4</sub>)  $\delta$  7.1 (broad peak), 3.5 (broad peak, 1), and 2.0–1.0 (overlapping multiplets, 13, singlet at 1.88, CH<sub>3</sub>). A trace of cyclohexanol was identified by peak enhancement. Yields of cyclohexyl nitrate and cyclohexene relative to benzaldehyde were determined by nmr analysis of the reaction mixtures using the signals at  $\delta$  4.9, 5.6, and 9.95, respectively. Several runs were carried out under a variety of conditions given in the Results.

**Cyclopropylphenylmethanol** was not stable to the reaction conditions. The alcohol was mixed with Ce(III), generated *in situ* from CAN and pinacol, and glpc analysis of the reaction mixture on column D revealed almost no starting alcohol and a new product with a longer retention time. This product was isolated by column chromatography using silica gel, and its nmr is similar to that reported for 4-phenylbut-3-en-1-ol.<sup>53</sup>

Details of the oxidation procedure and analysis for the other alcohols are given in Table IV.

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## Oxidation of Organic Compounds with Cerium(IV). XX. Abnormally Rapid Rate of Oxidative Cleavage of ( $\beta$ -Trimethylsilylethyl)phenylmethanol<sup>1</sup>

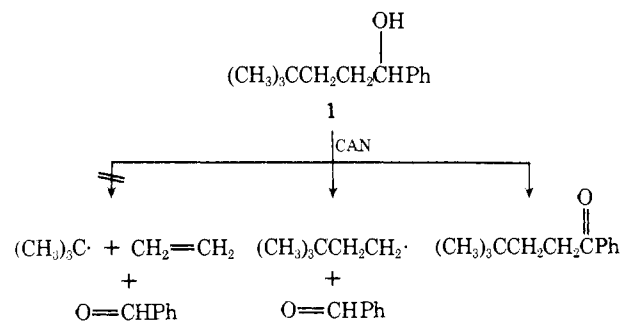
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**Abstract:** The ceric ammonium nitrate (CAN) oxidation of ( $\beta$ -*tert*-butylethyl)phenylmethanol (**1**) at 80° in 50% aqueous acetonitrile gave a ratio of oxidative cleavage to ketone formation, determined by measuring the relative yield of benzaldehyde to  $\beta$ -*tert*-butylethyl phenyl ketone, of  $3.27 \pm 0.07$ , and 44% of  $\beta$ -*tert*-butylethyl nitrate was produced. However, the CAN oxidation under identical conditions of ( $\beta$ -trimethylsilylethyl)phenylmethanol (**2**) gave a ratio of oxidative cleavage to ketone formation of  $166 \pm 26$ , a quantitative yield of ethylene, and a 50% yield (determined at 40°) of hexamethyldisiloxane. The ratio for **1** indicates that its rate constant for cleavage is that expected for formation of a primary alkyl radical. The large rate constant for cleavage of **2** could be a result of direct formation of the trimethylsilyl radical by two-bond cleavage or stabilization of the polar transition state of the cleavage reaction by the  $\beta$ -trimethylsilyl group.

Oxidation of secondary alcohols by cerium(IV) generally gives primarily products of oxidative cleavage, not ketone formation.<sup>1a,2</sup> 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.<sup>1,2</sup>

In an effort to find evidence for an oxidative cleavage which involves cleavage of two bonds simultaneously, we studied the ceric ammonium nitrate (CAN) oxidation of ( $\beta$ -*tert*-butylethyl)phenylmethanol (**1**). The ratio of cleavage to ketone formation, determined<sup>1a</sup> by measuring the relative yield of benzaldehyde to  $\beta$ -*tert*-butylethyl phenyl ketone, was found to be  $3.27 \pm 0.07$  at ca. 80° in 50% aqueous acetonitrile. The fact that this ratio is ca. 4, which is the ratio found for several other alkylphenylmethanols that produce ordinary primary radicals,<sup>1a</sup> indicates that no spe-



cial effects enhance the rate of cleavage of alcohol **1**. Also the detection of 44% (relative to benzaldehyde) of  $\beta$ -*tert*-butylethyl nitrate as a product indicates that only one bond of the alcohol was cleaved during the oxidation. Other possible products from this oxidation which were looked for but