

$^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  6.10 (1 H, dd,  $^2J_{\text{HF}} = 58.5$  Hz,  $^3J_{\text{HF}} = 11.4$  Hz, 2-H), 6.80-7.50 (4 H, m, ArH); MS (70 eV),  $m/e$  (relative intensity) 157 ( $\text{M}^+$ ); UV (EtOH) 278 nm. **30**:  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  5.98 (1 H, dd,  $^2J_{\text{HF}} = 61.2$  Hz,  $^3J_{\text{HF}} = 2.9$  Hz, 2-H), 6.70-7.45 (4 H, m, ArH); MS (70 eV),  $m/e$  (relative intensity) 157 ( $\text{M}^+$ ); UV (EtOH) 278 nm. **21**:  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  5.64 (1 H, dd,  $^2J_{\text{HF}} = 54.7$  Hz,  $^3J_{\text{HF}} = 11.5$  Hz, 3-H), 6.08 (1 H, dd,  $^2J_{\text{HF}} = 58$  Hz,  $^3J_{\text{HF}} = 11.5$  Hz, 2-H), 6.70-7.40 (3 H, m, ArH); MS (70 eV),  $m/e$  (relative intensity) 190 ( $\text{M}^+$ , 100), 192 (32); UV (EtOH) 286 nm. **31**: mp 82.5-83.5 °C;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  4.89 (1 H, ddd,  $^2J_{\text{HF}} = 54$  Hz,  $^3J_{\text{HF}} = 14.2$  Hz,  $^3J_{\text{HH}} = 5.2$  Hz, 3-H), 5.27 (1 H, ddd,  $^2J_{\text{HF}} = 60.8$  Hz,  $^3J_{\text{HF}} = 2.9$  Hz,  $^3J_{\text{HH}} = 5.2$  Hz, 2-H), 6.15-7.10 (3 H, m, ArH); MS (70 eV)  $m/e$  (relative intensity), 190 ( $\text{M}^+$  100), 192 (34); UV (EtOH) 286 nm.

**3-Bromo-,<sup>16b</sup> 3-bromo-5-chloro-,<sup>16b</sup> 3-chloro-,<sup>16b</sup> 3,5-dichloro-,<sup>16a</sup> 3-fluoro,<sup>31</sup> and 5-chloro-3-fluorobenzofuran** were prepared by dehydrohalogenation of **1**, **3**, **10**, **12**, **29**, and **31**, respectively, with *t*-BuOK in *t*-BuOH. The 5-chloro-3-fluoro derivative showed the following spectroscopic characteristics:  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  7.20-7.50 (3 H, m, ArH), 7.48 (1 H, d,  $^3J_{\text{HF}} = 4.5$  Hz, 2-H); MS (70 eV),  $m/e$  (relative intensity) 170 ( $\text{M}^+$ , 100), 172 (35); UV (EtOH) 287, 294 nm.

**18-Crown-6 ether (18C6)**, a commercial material (Fluka), was purified by crystallizing from *n*-hexane (mp 38.5-39.5 °C).

**Base-Solvent Solution.** *tert*-Butyl alcohol and ethyl alcohol (Erba RPE) were purified and dried as previously described.<sup>16b</sup> Solutions of alkoxide were obtained by reaction, under nitrogen, of freshly cut potassium with alcohol.

**Product Analysis.** A known amount of the dihalide was added, under strong stirring, to a solution of alkoxide in alcohol placed in a flask surrounded by a jacket for the circulation of the thermostating liquid. After a variable time (depending on the reactivity of the substrate) the reaction mixture was poured into water and the mixture extracted several times with petroleum ether. After the mixture was dried and the solvent evaporated, the crude reaction product was analyzed by  $^1\text{H}$  NMR and GLC (1.5  $\times$  0.002 m column packed with 1:1 15% bentone-didecylphthalate at 120 °C). In all the cases the corresponding 3-halogenobenzofuran was the exclusive final product from comparison with the authentic specimen.

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**Kinetic Studies.** Kinetic experiments were carried out by following spectrophotometrically the disappearance of the substrate at 288-320 nm. In all the cases the kinetic runs were carried out at a wavelength where no appreciable absorbance is exhibited by the final product. The base solution (2 mL) in a silica cell was placed in the thermostated compartment of the spectrophotometer. After about 20 min, the substrate solution (10-30  $\mu\text{L}$ ) in the same solvent was added. After being shaken rapidly, the cell was swiftly placed again in the spectrophotometer. The reference cell contained a solution of alkali alkoxide at the same concentration used in the kinetic run to compensate for the absorption exhibited by the alkoxide itself at 288-320 nm especially in the presence of the crown ether. The concentration of the substrate was in the range (4.5-9)  $\times 10^{-4}$  M, and the base concentration was 5  $\times 10^{-3}$  M for *t*-BuOK in *t*-BuOH and 2.7  $\times 10^{-2}$  M for EtOK in EtOH. At the end of each kinetic run it was checked that the UV spectrum of the reaction mixture was identical with that of the expected olefin.

**H-D Exchange Experiments.** A solution of ROK in ROH was added to a known amount of the dihalide **17** (the base-solvent molar ratio was 0.5). When the reaction was completed, the mixture was poured into water and the solution extracted with petroleum ether. The crude product, after the solvent evaporation, was analyzed by  $^1\text{H}$  NMR. In the spectrum in  $\text{CCl}_4$ , besides the multiplet relative to the final product and to the unreacted substrate, only a doublet at  $\delta$  6.15 ( $^2J_{\text{HF}} = 60$  Hz) of 2-H aliphatic proton of this substrate was observed, this showing no hydrogen incorporation at C-3 in the deuterated starting material.

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## Absolute Rate Constants for Reactions of Cumyloxy in Solution<sup>1</sup>

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Contribution from the Division of Chemistry, National Research Council, Ottawa, Ontario, Canada K1A 0R9. Received March 16, 1983

**Abstract:** Rate constants have been measured for reaction of  $\alpha$ -cumyloxy with 10 substrates including cumene and di- $\alpha$ -cumyl peroxide and for  $\beta$ -scission of  $\alpha$ -cumyloxy in solution by using laser flash photolysis techniques in conjunction with high-performance liquid chromatographic determination of product yields. Hydrogen atom abstraction from cumene and di- $\alpha$ -cumyl peroxide by  $\alpha$ -cumyloxy proceeds with  $E_x$  (kcal mol<sup>-1</sup>) = 2.4 and 5.7 and  $\log A_x$  (M<sup>-1</sup> s<sup>-1</sup>) = 8.1 and 9.4, respectively. The rate constant for  $\beta$ -scission of  $\alpha$ -cumyloxy obeys the equation  $\log k_\beta$  (s<sup>-1</sup>) = [(12.36  $\pm$  0.64) - (8.60  $\pm$  0.45)]/ $\theta$ , where  $\theta = 2.303RT$  kcal mol<sup>-1</sup>.

Alkoxy (RO $\cdot$ ), formed by decomposition of alkyl peroxides (ROOR), alkyl hydroperoxides (ROOH), and self-reaction of alkylperoxys (RO $_2$ ), are important transients in many biological<sup>3</sup> and atmospheric<sup>4</sup> oxidations. *tert*-Butoxy, because of its ease of

generation, has been the most thoroughly studied alkoxy in the gas and liquid phases. Higher homologues have, however, received some attention and studies on  $\alpha$ -cumyloxy have been of particular importance because of its involvement in cumene autoxidation.<sup>5</sup>

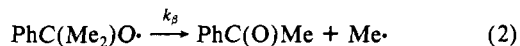
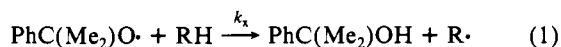
Walling and co-workers<sup>6</sup> were the first to study cumyloxy kinetics and obtained values of the rate constant ratio  $k_x/k_\beta$ , where

(1) Issued as NRCC No. 22461.  
 (2) NRCC summer student 1982.  
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$k_x$  is the rate constant for the hydrogen atom abstraction reaction (1) and  $k_\beta$  is the rate constant for the  $\beta$ -scission reaction (2), for several substrates (RH).



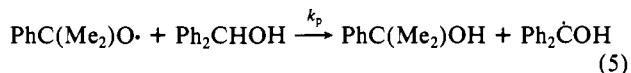
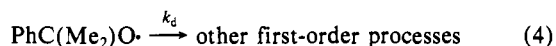
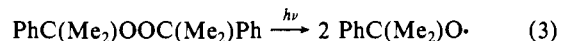
Subsequent studies<sup>7</sup> have confirmed and extended Walling's work and have lead to the determination of relative activation energies [ $E_\beta - E_x$  (kcal mol<sup>-1</sup>)] = 4.8 - 5.1 and 4.9 and preexponential factors  $\log(A_\beta/A_x)(\text{M}^{-1}) = 2.9$  and 4 for reactions of  $\text{PhC}(\text{Me}_2)\text{O}\cdot$  in  $\text{CCl}_4$  containing cyclohexane and in toluene, respectively.

Absolute values of  $A_x$  and  $E_x$  have not been reported for cumyloxy. There is, therefore, no data available to calculate absolute activation parameters for  $\beta$ -scission of this radical. We have, therefore, applied the laser flash photolysis technique in combination with the determination of product yields by high-performance liquid chromatography to the measurement of  $k_x$  and  $k_\beta$  for  $\text{PhC}(\text{Me}_2)\text{O}\cdot$  over a wide temperature range. The results of this study are reported here.

## Results

**Laser Flash Photolysis Experiments.** All experiments were carried out in deaerated solutions, using the pulses from a nitrogen laser (337.1 nm, ~8 ns, up to 10 mJ) for excitation and a detection system with nanosecond response to monitor transient absorptions. The experiments carried out in this study of cumyloxy are similar to those in a series of studies reported earlier for *tert*-butoxy.<sup>8</sup> The details of the kinetic analysis are also similar and are only described briefly here.

In these experiments di- $\alpha$ -cumyl peroxide, usually in benzene or chlorobenzene, is photodecomposed in the presence of a probe substrate and the substrate whose reactivity is being determined. The probe used was diphenylmethanol, which in earlier studies proved extremely convenient,<sup>8</sup> under these conditions the analyzing system is set at 540 nm, so as to monitor the formation of diphenylhydroxymethyl. The following reactions are expected to be of importance in the time scale examined,



as well as reactions 1 and 2.

The buildup of the signal at 540 nm follows clean first-order kinetics. Analysis of this buildup yields  $k_{\text{exptl}}$ , the first-order rate constant for signal buildup, such that:

$$k_{\text{exptl}} = k_o + k_p[\text{Ph}_2\text{CHOH}] + k_x[\text{RH}] \quad (6)$$

Thus, the values of  $k_x$  are easily obtained by keeping the probe concentration constant and changing the substrate concentration. A plot of  $k_{\text{exptl}}$  vs. [RH] then yields  $k_x$  from the slope. Radical-radical reactions do not need to be taken into consideration

Table I. Rate Constants for the Reaction of Cumyloxy and *tert*-Butoxy with Various Substrates

substrate	$k_x(\text{cumyloxy})^a$	solvent	$k_x(\text{tert-butoxy})^{b,c}$
cumene	$(2.27 \pm 0.35) \times 10^6$	chlorobenzene	$8.7 \times 10^6^d$
diphenylmethanol	$(1.18 \pm 0.19) \times 10^7$	chlorobenzene	$7.2 \times 10^6^e$
tetrahydrofuran	$(1.04 \pm 0.17) \times 10^7$	benzene	$8.3 \times 10^6^d$
cyclohexene	$(1.01 \pm 0.11) \times 10^7$	benzene	$5.8 \times 10^6^e$
oct-1-ene	$(4.59 \pm 0.80) \times 10^6$	benzene	$1.5 \times 10^6^e$
1,3-cyclooctadiene	$(2.30 \pm 0.70) \times 10^6$	benzene	$3.6 \times 10^6^e$
2,5-dimethyl-2,4-hexadiene	$(2.64 \pm 0.62) \times 10^6$	benzene	-
cyclohexane	$(2.04 \pm 0.73) \times 10^6$	benzene	$1.6 \times 10^6^e$
phenol	$(2.25 \pm 0.07) \times 10^6$	chlorobenzene	$3.3 \times 10^6^d$

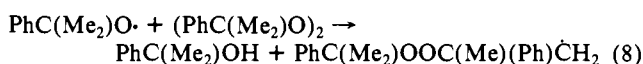
<sup>a</sup> In  $\text{M}^{-1} \text{s}^{-1}$ , at 300 K. <sup>b</sup> In  $\text{M}^{-1} \text{s}^{-1}$ , at either 295 or 300 K, as indicated. <sup>c</sup> Taken from ref 8, usually in benzene-di-*tert*-butyl peroxide mixtures. <sup>d</sup> At 295 K. <sup>e</sup> At 300 K.

in this time scale, provided that suitable control experiments are carried out in order to adjust the laser dose.<sup>8b</sup> Reactions of other radicals such as  $\text{CH}_3\cdot$  are not expected to be of importance in this time scale.<sup>8b</sup> Table I gives the values of  $k_x$  obtained for several representative substrates, along with the rate constants for *tert*-butoxy, whenever available.

The values of  $k_o$  can be obtained from the intercepts of plots of  $k_{\text{exptl}}$  vs.  $[\text{Ph}_2\text{CHOH}]$  in experiments with variable diphenylmethanol, and in the absence of substrate RH. The values of  $k_o$  are given by

$$k_o = k_\beta + k_d \quad (7)$$

where  $k_d$  incorporates all first-order modes of decay in any given solvent, with the exception of  $\beta$ -scission that has been included explicitly. In the case of *tert*-butoxy, we usually did not examine the  $k_o$  values very extensively, since they were mainly determined by reactions with the solvent.<sup>8a,b</sup> By contrast, the case of cumyloxy,  $\beta$ -scission is well-known to be an important reaction mode and, indeed, the predominant component in  $k_o$ . Thus, the values of  $k_\beta$  can be obtained from the intercepts if an adequate correction to account for  $k_d$  can be made. In our case, the radicals are not expected to react with solvents such as benzene or chlorobenzene; however, they will abstract hydrogen from the parent peroxide, though this reaction is expected to be relatively minor, since only primary C-H bonds are available, i.e.,



Thus, the relative contribution of  $k_\beta$  and  $k_d$  to  $k_o$  is expected to be identical with the relative contribution of acetophenone and cumyl alcohol to the total products. These have also been determined in this study (see below), and all the information is available. Over the temperature range used in the laser studies the contribution of  $k_\beta$  to  $k_o$  ranged from ~94% at 357 K to 40% at 234 K for 1.17 M peroxide. The Arrhenius parameters for the  $\beta$ -scission reaction were obtained from a combined analysis of data obtained by two different techniques and is presented under Discussion. The values of  $k_\beta$  obtained by the laser technique are subject to more error at the lower temperatures, because the intercept of the  $k_{\text{exptl}}$  plots is very small under these conditions.

The temperature dependence of intermolecular reactions was examined for two substrates, cumene and diphenylmethanol. For cumene, data in the 230-330 K range yields

$$\log k_x(\text{M}^{-1} \text{s}^{-1}) = [(8.08 \pm 0.47) - (2.36 \pm 0.58)]/\theta \quad (9)$$

where  $\theta = 2.3RT$  in kcal/mol, and the errors are quoted as  $\pm 2\sigma$ . For diphenylmethanol in the 222-343 K range we obtained:  $\log k_x(\text{M}^{-1} \text{s}^{-1}) = [(9.26 \pm 0.61) - (2.98 \pm 0.78)]/\theta$ . However, we find significant scattering of the data for diphenylmethanol at the higher temperatures probably reflecting the fact that  $k_\beta$  approaches  $10^7 \text{ s}^{-1}$ , which makes the experimental measurements quite dif-

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Table II. Product Yields and Relative Rate Constants ( $k_x/k_\beta$ ) for Reaction of Cumyloxy with Cumene (A) and Di- $\alpha$ -cumyl Peroxide<sup>a</sup> (B)

temp, K	system	acetophenone, mM	$\alpha$ -cumyl alcohol, mM	$k_x/k_\beta$ , M <sup>-1</sup>
303	A	0.31	3.6	1.6
313	A	1.18	9.0	1.1
323	A	0.64	3.9	0.85
333	A	1.0	7.5	1.05
353	A	0.6	1.8	0.42
364	A	4.2	6.2	0.2
373	A	10.0	9.5	0.13
395	A	16.0	8.5	0.074
238	B	1.55	1.55	1.0
254	B	3.0	5.10	0.59
270	B	3.6	1.12	0.31
285	B	3.5	1.1	0.31
302	B	7.3	1.17	0.16
324	B	4.8	0.75	0.16
353	B	5.0	0.57	0.114
373	B	6.75	0.6	0.09

<sup>a</sup> 1 M in chlorobenzene.

ficult. A better estimate weighing more heavily the data at the lower temperatures and concentrating on the 222–315 K range gives the more reasonable Arrhenius equation  $\log k_x(\text{M}^{-1} \text{s}^{-1}) = [(8.8 \pm 0.6) - (2.6 \pm 0.6)]/\theta$ . For both systems the solvent was chlorobenzene, and the parameters reported have been corrected to take into account the temperature coefficient of the solvent's density.

It should be noted that all intermolecular rate constants measured by using the laser techniques described here refer to molecular reactivity; that is, they include all possible modes and sites of attack. This consideration is particularly important in the case of olefins, where abstraction (usually allylic) and addition reactions are included in  $k_x$ .

**Product Studies.** Thermolysis of di- $\alpha$ -cumyl hyponitrite (~10 mM) and thermolysis and photolysis of di- $\alpha$ -cumyl peroxide (~15 mM) in deaerated cumene (7.17 M) and chlorobenzene containing di-cumyl peroxide (1 M) from 238 to 395 K gave acetophenone (K) and  $\alpha$ -cumyl alcohol (A) in the yields given in Table II. Values of the rate constant ratio  $k_x/k_\beta$  were calculated from  $[A]/[K][RH]$ . An Arrhenius plot of the data for di- $\alpha$ -cumyl peroxide gave  $\log(k_x/k_\beta)(\text{M}) = [(-3.0 \pm 0.5) \pm 0.5] + (2.9 \pm 0.4)/\theta$ . The data for cumene could also be treated in a similar way; however, a combined analysis including product and laser data was preferred since it covers a greatly extended temperature range and leads to a significant decrease in the error limits. This analysis is presented under Discussion.

## Discussion

It was found that the most satisfactory way of combining the  $\beta$ -scission data obtained from laser and product studies was to process them to the point of deriving absolute values of  $k_\beta$  from both sets of data. In the case of the laser data the values of  $k_o$  are corrected according to the alcohol-acetophenone ratios in that particular solvent. In general alcohol yields under these conditions are low (see Table II), and the correction should not be an important source of error. The main source of error results from the small value of the intercepts in plots of  $k_{\text{expt}}$  vs. [diphenylmethanol] at the lower temperatures.

Product studies yield values of  $k_x/k_\beta$ , where  $k_x$  refers to abstraction from the solvent, which in this case was cumene (see Table II). Since the Arrhenius parameters have been determined for this substrate by using laser photolysis, it is straightforward to obtain  $k_\beta$  values. It should be noted that in this case the errors are larger at the higher temperatures, because under these conditions cumyloxy decays predominantly via  $\beta$ -scission, and eventually the alcohol ratios become too low for accurate determination. Figure 1 shows an Arrhenius plot combining the data from both sets of experiments, where the assumption has been made that the difference in solvent (chlorobenzene vs. cumene) can be ig-

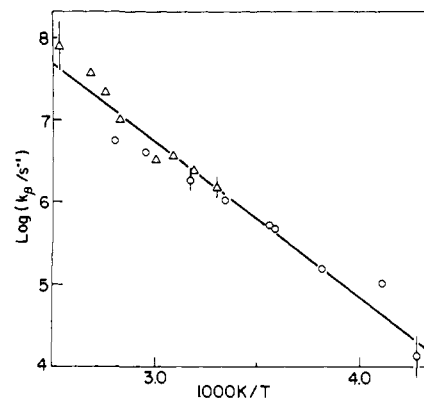


Figure 1. Arrhenius plot for the  $\beta$ -scission of cumyloxy, using data from product studies ( $\Delta$ ) and laser techniques ( $\circ$ ).

nored. The parameters obtained in the 234 to 395 K range lead to

$$\log k_\beta(\text{s}^{-1}) = [(12.36 \pm 0.64) - (8.60 \pm 0.45)]/\theta \quad (10)$$

The  $A$  factor and activation energy for  $\beta$ -scission of cumyloxy are approximately 1.4 log units and 6.7 kcal mol<sup>-1</sup> less than the Arrhenius parameters estimated by Choo and Benson<sup>9</sup> for decomposition of *tert*-butoxy in the gas phase ( $\log A_\beta(\text{M}^{-1} \text{s}^{-1}) = 14.1$ ,  $E_\beta = 15.3$  kcal mol<sup>-1</sup>).<sup>10</sup> The difference in preexponential factor can be attributed to a difference in the stiffness of the transition state for decomposition of the two radicals, which in the case of  $\alpha$ -cumyloxy will involve some resonance stabilization in the transition configuration. This leads to a reduction of the activation energy and a loss of entropy of activation resulting from an increase in the barrier to internal rotation, which stiffens the transition state. Our results suggest an entropy loss of ~8.3 cal deg<sup>-1</sup> mol<sup>-1</sup> relative to the value that can be calculated from Choo and Benson's<sup>9</sup> preexponential factor. It is interesting to note that  $\Delta\Delta S^\ddagger$  for scission of *tert*-butoxy and cumyloxy is very similar to the difference for pyrolysis of neopentane and *tert*-butylbenzene.<sup>12</sup>

The  $A$  factor for reaction of cumene with cumyloxy of 8.1 log units is in good agreement with the assigned value of 8.4 on the basis of the probable change in entropy for abstraction of a tertiary benzylic hydrogen by a polyatomic radical<sup>13</sup> and is slightly lower than the value of 8.7 reported for reaction of cumylperoxy with cumene.<sup>14</sup> The difference in the activation energies for reaction of cumene with cumyloxy and cumylperoxy of 11 kcal mol<sup>-1</sup> is close to the difference in the strengths of the O–H bonds in the reaction products, cumyl alcohol ( $D_{\text{RO-H}} \sim 102$ –103 kcal mol<sup>-1</sup>) and cumene hydroperoxide ( $D_{\text{ROO-H}} \sim 90$  kcal mol<sup>-1</sup>).

The overall  $A$  factor for di- $\alpha$ -cumyl peroxide of 9.5 log units is also in good agreement with the assigned value for the overall  $\log A$  of 10.1 for 12 primary aliphatic hydrogens.<sup>13</sup>

From the relative data of Walling et al.<sup>6</sup> and our absolute parameters for  $\beta$ -scission of cumyloxy values of  $\log A_x(\text{M}^{-1} \text{s}^{-1}) = 9.4$  and  $8.4$  and  $E_x(\text{kcal mol}^{-1}) = 3.5$ – $3.8$  and  $3.7$  can be calculated for reaction of cyclohexane and toluene with cumyloxy, respectively, parameters that seem reasonable in the light of the absolute activation parameters for cumene and our understanding of the transition state for this reaction.

## Experimental Section

**Materials.** Benzene, cumene, and chlorobenzene were purified by washing with sulfuric acid, sodium bicarbonate solution, and water. They were then dried and distilled from CaH<sub>2</sub>. Di- $\alpha$ -cumyl peroxide was

(9) Choo, K. Y.; Benson, S. W. *Int. J. Chem. Kinet.* **1981**, *13*, 833–844.

(10) Somewhat higher values have been estimated by Batt and Robinson<sup>11</sup> ( $\log A_\beta(\text{M}^{-1} \text{s}^{-1}) = 14.9$ ,  $E_\beta = 16.6$  kcal mol<sup>-1</sup>).

(11) Batt, L.; Robinson, G. N. *Int. J. Chem. Kinet.* **1982**, *14*, 1053–1055.

(12) Benson, S. W.; O'Neal, H. E. "Kinetic Data on Gas Phase Unimolecular Reactions", NSRDS-NBS 21, 1970.

(13) Hendry, D. G.; Mill, T.; Piszkiwicz, L.; Howard, J. A.; Eigenmann, H. K. *J. Phys. Chem. Ref. Data* **1974**, *3*, 937–978.

(14) Howard, J. A.; Chenier, J. H. B.; Holden, D. A. *Can. J. Chem.* **1978**, *56*, 170–175.

recrystallized three times from methanol. Di- $\alpha$ -cumyl hyponitrite was prepared from  $\alpha$ -cumyl bromide and silver hyponitrite by the method of Kiefer and Traylor.<sup>15</sup>

**Product Yields.** Yields of acetophenone and  $\alpha$ -cumyl alcohol from decomposition of di-cumyl peroxide and di-cumyl hyponitrite were determined by high-performance liquid chromatography using a Varian 5000 liquid chromatograph controlled by a Vista 401 chromatography data system. The chromatograph was equipped with a reverse-phase column, and the eluting solvent was a mixture of acetonitrile and water. The solvent initially contained 40% acetonitrile, and the percentage of this constituent was gradually increased to 100%.

(15) Kiefer, H.; Traylor, T. G. *Tetrahedron Lett.* **1966**, 6163-6168.

(16) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, 102, 7747-7754.

**Laser Flash photolysis.** All experiments were carried out in deaerated samples contained in Suprasil cells made of  $7 \times 3$  mm<sup>2</sup> rectangular tubing. A Molecron UV-24 nitrogen laser, delivering pulses at 337.1 nm, was used for excitation. The transient signals were initially recorded by a Tektronix 7912 transient digitizer and then transferred to a PDP-11/23 computer, which was also used to control the experiment, for data processing, as well as to provide suitable storage and hardcopy facilities. Further details have been reported elsewhere.<sup>16</sup>

**Registry No.** (PhC(Me)<sub>2</sub>O)<sub>2</sub>, 80-43-3; PhC(Me)<sub>2</sub>O, 16812-36-5; H, 1333-74-0; cumene, 98-82-8; diphenylmethanol, 91-01-0; tetrahydrofuran, 109-99-9; cyclohexene, 110-83-8; 1-octene, 111-66-0; 1,3-cyclooctadiene, 1700-10-3; cyclohexane, 110-82-7; phenol, 108-95-2; di- $\alpha$ -cumyl hyponitrite, 21799-93-9;  $\alpha$ -cumyl bromide, 3575-19-7; silver hyponitrite, 7784-04-5.

## Electronic Absorption and Circular Dichroism Spectra of the Perturbed Coplanar *cis*-Diene Chromophore in Deuterium- and Methyl-Substituted 7,7-Dimethylbicyclo[4.1.1]octa-2,4-dienes

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**Abstract:** The optically active monodeuterated 7,7-dimethylbicyclo[4.1.1]octa-2,4-dienes **6** and **8** have been prepared with known absolute configuration from (+)-nopinone. Access to their methyl congeners **7** and **9** has been achieved from (+)- $\alpha$ -pinene and (+)-nopinone, respectively. In **6** and **8**, the chirality is due solely to isotopic substitution. The contributions of the C-D and C-CH<sub>3</sub> groups to the observed absorption and circular dichroism spectra are analyzed. In particular, attention is directed to the planar *cis*-1,3-diene unit in **6-9**, the resultant zero dihedral angle between the C<sub>2</sub>-C<sub>3</sub> and C<sub>4</sub>-C<sub>5</sub> bonds at equilibrium, and the consequences of this unique fixed geometry.

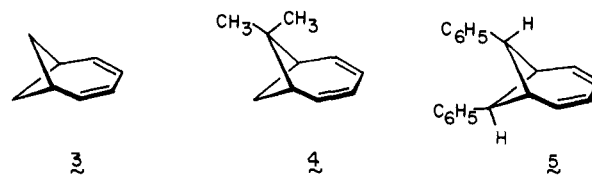
The chiroptical properties of chiral, *cisoid*, *nonplanar* 1,3-dienes have been extensively studied over the years.<sup>2</sup> The early analyses suggested that the particular sign of the observed long-wavelength Cotton effects is controlled largely by the helicity of the inherently dissymmetric skewed diene chromophore,<sup>3</sup> but subsequently chiroptical contributions by homoallylic and bis(homoallylic) substituents, both axial<sup>4</sup> and equatorial,<sup>5</sup> were found to be substantial.<sup>6</sup> Unfortunately, competing chirality contributions resulting from dihedral angle alterations in conformationally flexible systems can often lead to ambiguous results.<sup>5</sup>

In the present study, we give attention to planar, inflexible 1,3-diene systems whose chirality is dependent solely upon deuterium or methyl substitution at the  $\alpha$  and  $\beta$  positions. Only recently has <sup>2</sup>H-induced perturbation of isolated<sup>7</sup> and homoconjugated carbon-carbon double bonds<sup>8,9</sup> been given some attention.

No prior assessment appears to have been made of this theoretically interesting combination of structural features, although investigation of the more remotely perturbed "quasi-planar" dienes **1**<sup>10</sup> and **2**<sup>11</sup> has been recently completed.



In order to isolate the effect of deuterium or methyl perturbation from other chiroptical influences generally associated with chiral molecules, it becomes highly desirable to deal with compounds that possess an achiral skeleton. In this manner, the chirality of the substrate is due solely to the substituent. This criterion is best met by ring systems endowed with axes or planes of symmetry, provided that all symmetry planes are destroyed upon substitution. We considered our purposes to be best served by the bicyclo[4.1.1]octa-2,4-diene framework (**3**), where strong interaction ( $\beta$



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