NH_4OAc (5.14 g, 66.7 mmol) in H_2O (17 mL) to 20% aqueous $TiCl_3$ (1.715 g, 11.1 mmol, 9 mL of H_2O) under argon. This buffered solution was added to a solution of 1-acetyl-4-(nitromethyl)-1-cyclohexene (510 mg, 2.78 mmol), sodium methoxide (150 mg, 2.78 mmol), and methanol (6 mL) and stirred under argon at room temperature for 3.5 h. Dilution with Et_2O (50 mL) and extraction with Et_2O (2 × 50 mL) gave a light yellow organic layer that was washed with saturated $NaHCO_3$ (2 × 50 mL) and brine (1 × 50 mL), dried over Na_2SO_4, and filtered, and the solvent was removed in vacuo to give an orange oil. Chromatotron separation (1:1 hexane/ethyl acetate) gave 166 mg (39%) of product. Evaporative distillation (46–48 °C/0.04–0.02 mm) gave an analytical sample: ^1H NMR ($CDCl_3$) δ 1.6–1.8 (m, 2), 2.0–2.2 (m, 1), 2.30 (s, 3, $COCH_3$), 2.35–2.6 (m, 4), 6.92 (m, 1, $=CH$), 9.73 (s, 1, CHO); IR (neat) 1725 (CHO), 1664 ($C{=}O$) cm^{-1}. Anal. ($C_9H_{12}O_2$) C, H.

1-Acetyl-4-(nitromethyl)cyclohexane. To a Fischer-Porter bottle was added 1-acetyl-4-(nitromethyl)cyclohexane (734 mg, 4.01 mmol), absolute EtOH (20 mL), and PtO_2 (45 mg, 0.2 mmol). The bomb was evacuated and filled three times with H_2. The third time the bomb was charged with 43 psi of H_2, and the contents were stirred 22.5 h at 60 °C. The contents of the reactor were cooled, diluted with Et_2O (50 mL), gravity filtered, dried with $MgSO_4$, filtered again, and concentrated in vacuo. The yellow oil was purified by Chromatotron (1:3 hexane/ethyl acetate) to give 370 mg (50%, R_f 0.53) of product as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.38 (m, 2), 1.65 (m, 4), 1.96 (m, 2), 2.16 (s, 3, $COCH_3$), 2.32 (m, 1), 2.57 (quint, J = 5.1 Hz, 1, CHCO), 4.28 (d, J = 7.4 Hz, 2, CH_2NO_2); IR (neat) 1710 ($C{=}O$), 1550 (CNO_2) cm^{-1}. An analytical sample was obtained by evaporative distillation (62 °C/0.025 mm). Anal. ($C_9H_{15}NO_3$) C, H, N.

Acknowledgment. This research was supported by Grant No. CHE8200522 from the National Science Foundation. High-field NMR spectra were obtained on instruments in the Colorado State University Regional NMR Center funded by National Science Foundation Grant No. CHE7818581. We thank Paige Loomis for technical assistance.

Registry No. **1**, 33482-84-7; **2**, 4117-50-4; *trans*-$CH_3C(O)CH_2CH{=}CH(CH_2)2NO_2$, 90295-76-4; *trans,trans*-$(CH_3C(O)CH_2CH{=}CHCH_2)_2CHNO_2$, 90341-46-1; *trans*-$CH_3C(O)CH_2CH{=}CHCH_2CH(NO_2)CH_3$, 90295-77-5; *trans,trans*-$(CH_3C(O)CH_2CH{=}CHCH_2)_2C(NO_2)CH_3$, 90295-78-6; *trans*-$CH_3C(O)CH_2CH{=}CHCH_2C(CH_3)_2NO_2$, 90295-79-7; *trans*-$CH_3C(O)CH_2C(CH_3){=}C(CH_3)_2NO_2$, 90295-80-0; $CH_3C(O)C({=}CH_2)(CH_2)_2NO_2$, 90295-84-4; $CH_3C(O)C({=}CH_2)CH(OMe)CH_2NO_2$, 90295-85-5; $CH_3C(O)C({=}CH_2)CH(t\text{-}BuO)CH_2NO_2$, 90295-86-6; $CH_3C(O)C({=}CHBr)(CH_2)_2NO_2$, 90295-87-7; $CH_2{=}CHCH{=}CH_2$, 106-99-0; $CH_2{=}C(CH_3)C(CH_3){=}CH_2$, 513-81-5; $CH_2{=}C{=}CH_2$, 463-49-0; $CH_2{=}C{=}CHOCH_3$, 13169-00-1; $t\text{-}BuOCH{=}C{=}CH_2$, 33721-28-7; $CH_2{=}C{=}CHBr$, 10024-18-7; $CH_2NO_2^-$, 18137-96-7; $CH_3CHNO_2^-$, 25590-58-3; $(CH_3)_2CNO_2^-$, 20846-00-8; $NaCo(CO)_4$, 14878-28-5; $Co_2(CO)_8$, 10210-68-1; MeI, 74-88-4; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; 1-acetyl-4-(nitromethyl)-1-cyclohexene, 90295-81-1; *cis*-1-acetyl-4-(nitromethyl)-2,3-dehydrodecalin, 90295-82-2; 2-(nitromethyl)-1-[(acetylmethyl)methylene]cyclohexane, 90295-83-3; 1,3-cyclohexadiene, 592-57-4; 1,2,3,4,4a,8a-hexahydronaphthalene, 62690-62-4; 1-vinyl-1-cyclohexene, 2622-21-1; 1-acetyl-6-methyldecalin-1,3-diene, 90295-88-8; 6-methyldecalin-1,3-diene, 90295-89-9; 2-acetyl-$\Delta^{2,4}$-cholestadiene, 90341-54-1; $\Delta^{2,4}$-cholestadiene, 4117-50-4; 1-(1-hydroxyethyl)-4-(nitromethyl)cyclohexene, 90295-90-2; 1-(1-hydroxyethyl)-4-(aminomethyl)cyclohexene, 90295-91-3; 3-(4-acetyl-3-cyclohexyl)-4,5-dicarbomethoxyisoxazole, 90295-92-4; 4-acetyl-3-cyclohexenecarboxaldehyde, 90295-93-5; 1-acetyl-4-(nitromethyl)cyclohexane, 90295-94-6.

Relative Reactivities of Alkylbenzenes and Related Compounds toward Ozone. The Mechanism of Ozonation at Benzylic Positions

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Four monoalkylbenzenes and selected polyphenylalkanes, fluorenes, and partially reduced anthracenes and phenanthrenes were ozonized at 25 °C in dichloromethane, and relative reactivities were determined. These reactivities can be divided into the percent of ring ozonation plus the percent of reaction at the benzylic position (which yields hydrotrioxides) by comparison with related systems that undergo only the former reaction. (For example, the relative reactivities of toluene and *tert*-butylbenzene can be compared to determine the relative reactivity of toluene's benzylic position.) Introduction of either one or two methyl or phenyl groups at the exocyclic position of toluene markedly increases benzylic reactivity. Although 9,10-dihydroanthracene derivatives are structurally similar to diphenylmethane, their benzylic reactivity toward ozone is some 50 times greater on a per hydrogen basis; this is explicable in terms of the greater ease of achieving a planar transition state in the former case and the resultant greater delocalization in the benzylic intermediate. The relatively modest amount of benzylic reaction for fluorene leads us to propose that the intermediate involved in hydrotrioxide formation is a carbocationic species, rather than a free radical, in agreement with the recent suggestion of Nangia and Benson.

We recently reported a study of the ozonation of cumene in which the total reactivity was separated into ring ozonation and attack on the side-chain benzylic hydrogen.[2,3] Attack at the benzylic position produces cumyl hydrotrioxide, $PhCMe_2OOOH$, which decomposes above about −20 °C to produce free radicals. In an effort to understand the factors that affect the production of hydrotrioxides in the ozonation of aralkyl compounds, we here report a study of the ozonation of four monoalkyl benzenes and several related compounds.

The ozonation of alkyl- and polyalkylbenzenes has been reported by several groups.[4-6] The most extensive study

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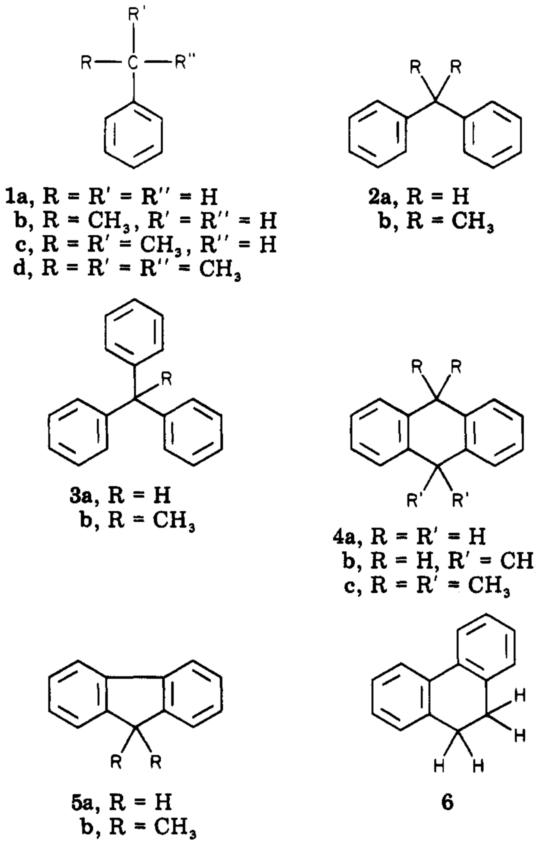

Figure 1. Systems studied.

was that of Nakagawa, Andrews, and Keefer,[5] which reveals some general trends. Increasing the number of methyl substituents attached to a benzene ring monotonically increases the total reactivity. Bernatek, Karlsen, and Ledaal estimate that each additional methyl group approximately doubles reactivity.[6] Other alkyl groups do not exhibit the same rate-enhancing effect throughout the entire range of substitution patterns, a result which has been attributed to steric factors.[5] Although not stressed in the original report by Nakagawa et al., a significant difference exists among the reactivities of monoalkylbenzenes. Cumene and ethylbenzene are more reactive than toluene which is more reactive than *tert*-butylbenzene.[5] Since the electron-donating ability of these substituents is approximately equal, one may infer that the rates of ring ozonation should be quite similar; it therefore is attractive to equate this rate variation with differing rates of ozonation at the benzylic position to yield hydrotrioxides.

We here report the total reactivity of several aralkyl hydrocarbons (shown in Figure 1) toward ozone. By the use of suitable model compounds, we have attempted to separate ring and benzylic reactivity.

Experimental Section

Materials. Compounds **1a**–**d**, **2a**–**b**, **3a**, **4a**, **5a**, **6**, *p*-di-*tert*-butylbenzene, indan, tetralin, biphenyl, *p*-dichlorobenzene, *p*-diiodobenzene, and phenanthrene were the best available commercial grades and were purified by standard methods. The additional hydrocarbons utilized in this study were prepared in accord with published procedures as follows: **3b**,[7] **4b**,[8] **4c**,[9] and **5b**.[10] Physical properties agreed with literature values. No contaminants could be detected in any of these compounds by gas chromatography on a capillary column, and purities are estimated to be in excess of 99%. Nanograde dichloromethane (Mallinckrodt) was used. Ozone–oxygen mixtures were prepared by flowing oxygen through a Welsbach T-23 ozone generator; ozone was generated at 0.0035 mmol/min.

Analysis. Analyses of reaction mixtures were carried out on a Varian Model 3700 gas chromatograph and CDS 111 electronic integrator. An SE-30 capillary column (15 m, fused silica) was used in all runs.

Results

The identification and quantification of the products of ozonation of the simple alkylbenzenes is difficult because of the further reaction of the primary products.[11] The products we have detected are as follows. Diphenylmethane (**2a**) yields benzophenone in 57 ± 2% yield. Triphenylmethane (**3a**) gives rise to benzophenone and triphenylmethanol in a ratio of 2.6 ± 0.1:1; the total yield of these two products was 51 ± 2%. Both 9,10-anthraquinone and anthracene were produced in the ozonation of 9,10-dihydroanthracene (**4a**); the mass balance and the ratio of the two products was time dependent, with a larger 9,10-anthraquinone/anthracene ratio at longer times since anthracene itself undergoes ozonation to produce the quinone. (Similar findings have been observed by Copeland, Dean, and McNeil.[12]) We observe a combined yield of the two products of 60 ± 4% at low conversions, somewhat higher than was found by Copeland et al.[12] Fluorene **5a** gave a 27 ± 3% yield of fluorenone, in good agreement with the range of values from 19 to 24% reported by Batterbee and Bailey under conditions of varying solvent and temperature.[13] (Earlier workers had reported a yield of fluorenone of only 7%.[14]) In all of the above cases the molar yields of alcohols and carbonyl compounds are much less than the moles of hydrocarbon consumed. Most of this difference is due to ring ozonation of the hydrocarbon; however, some ring ozonation of the alcohol and carbonyl products probably also occurs.

We used direct competitive techniques to evaluate relative reactivities following the rates of disappearance of two hydrocarbons, A and B, in competition and using eq I to calculate relative rate constants. Solutions containing

$$k_A/k_B = \log [A]/[A]_0/\log[B]/[B]_0 \qquad \text{(I)}$$

pairs of hydrocarbons were prepared in dichloromethane; the average total molarity was approximately 0.1 M. Aliquots of these solutions were treated directly with ozone in an oxygen stream for varying lengths of time at 25 ± 1 °C. Because of the ability of ozone to react with most organic substrates, no internal GC standard was added to the reaction mixture until 30 min to 3 h after ozonation ended and nitrogen had been bubbled through the system to purge any traces of unreacted ozone. The internal standards were dichlorobenzene, p-diiodobenzene, or phenanthrene, chosen so as to maximize GC separability.

The large majority of the hydrocarbons investigated were studied in competitive ozonation with *p*-di-*tert*-butylbenzene, chosen because of favorable GC separability from the other hydrocarbons and the internal standards. The reactivity of this compound, which is entirely due to ring ozonation, is comparable in most cases to that of the

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Table I. Relative Rate Constants for Pairs of Reactants toward Ozone in Dichloromethane at 25 °C

PAH_1	PAH_2	t, min	k_1/k_2[b]
2a	DTBB[a]	90	1.74
		135	1.87, 1.60, 1.85
2b	DTBB[a]	90	0.65, 0.64, 0.62
		120	0.65, 0.64
3b	DTBB[a]	90	0.87, 0.78
		120	0.84, 0.90
		150	0.91
4b	**5a**	60	5.6, 6.5
		90	6.2, 6.6
		150	6.5

[a] Di-*tert*-butylbenzene. [b] Relative rate constants for reaction of PAH_1 vs. PAH_2.

Table II. Relative Reactivities of Monoalkylated Benzenes in Dichloromethane toward Ozone at 25 °C

hydrocarbon	k_{tot}[a]	benzylic reactn,[b] %	k_{tot} (lit.)[c]
toluene	1.05 ± 0.01	49	1.06
ethylbenzene	1.86 ± 0.04	71	2.17
cumene	1.86 ± 0.16	71	2.23
tert-butylbenzene	0.54 ± 0.03		0.44
p-di-*tert*-butylbenzene	(1.00)	0	

[a] All rates relative to *p*-di-*tert*-butylbenzene. [b] Calculated from eq 6. [c] Reference 5.

hydrocarbons under investigation. Two related systems, 9,10-dihydroanthracene (**4a**) and 9,9-dimethyl-9,10-dihydroanthracene (**4b**), proved to be too reactive for direct competition against this reference, and these compounds were run relative to fluorene (**5a**).

All reactions were run in five or more replicates. Reaction times varied from 1 to 3 h. Hydrocarbon disappearance was usually limited to 16–65%, but in a few runs up to 75% hydrocarbon loss was observed. No variation within the limits of experimental uncertainty was observed for relative rates of disappearance as a function of reaction time; Table I presents representative data. Table II summarizes the relative rates of disappearance of the four monoalkylbenzenes. Relative rates of disappearance of the remaining compounds are given in Table III.

Discussion

The substrates studied here can undergo ring ozonation and/or ozonation at the benzylic position. The products from ring ozonation were not characterized in most cases; however, products analogous to those reported for the ozonation of benzene should be formed.[11] The initial products from side-chain ozonation are presumed to be the hydrotrioxides, eq 1, which at temperatures above about −20 °C undergo decomposition to form alcohols, reactions 2–4.[3] Also, when the alcohol is primary or secondary,

$$R\text{-}H + O_3 \rightarrow ROOOH \quad (1)$$

$$ROOOH \rightarrow RO\cdot + HOO\cdot \quad (2)$$

$$RO\cdot + ROOOH \rightarrow ROH + ROOO\cdot \quad (3)$$

$$ROOO\cdot \rightarrow RO\cdot + O_2 \quad (4)$$

further reaction with ozone is very likely, since carbinol hydrogens are approximately 100 more reactive than the corresponding hydrogens in hydrocarbons.[15]

Table III. Relative Reactivities of Other Hydrocarbons in Dichloromethane toward Ozone at 25 °C

hydrocarbon	k_{tot}[a]	benzylic reactn, %
diphenylmethane (**2a**)	1.77 ± 0.12	63.8
2,2-diphenylpropane (**2b**)	0.64 ± 0.01	(0)
triphenylmethane (**3a**)	4.07 ± 0.37	78.9
1,1,1-triphenylethane (**3b**)	0.86 ± 0.05	(0)
9,10-dihydroanthracene (**4a**)[b]	104 ± 16	99.2
9,9-dimethyl-9,10-dihydroanthracene (**4b**)[b]	57.0 ± 3.1	98.6
9,9,10,10-tetramethyl-9,10-dihydroanthracene (**4c**)	0.82 ± 0.03	(0)
fluorene (**5a**)	9.08 ± 0.55	38.6
9,9-dimethylfluorene (**5b**)	5.58 ± 0.32	(0)
9,10-dihydrophenanthrene (**6**)	7.23 ± 0.60	80–90[c]

[a] All rates relative to *p*-di-*tert*-butylbenzene, except as indicated. [b] Run vs. fluorene. [c] Estimated value based on the reactivities of ethylbenzene and biphenyl.

These reactions produce radicals, but it is unlikely that radical-induced destruction of the aromatic hydrocarbons contributes appreciably to the relative rates we observe. Several lines of evidence support this statement. (1) When cumene is allowed to react with ozone, the excess ozone removed, and the cumyl hydrotrioxide allowed to decompose, the primary products are cumyl alcohol and cumyl hydroperoxide.[3] Both these species would react with either alkoxyl or peroxyl radicals faster than does cumene;[16] thus, the products protect the hydrocarbon substrate against radical attack. Since ozone is less selective than either alkoxyl or peroxyl radicals, this protection is much less true for ozone. (2) The system reported here uses continuously flowing ozone, whereas our previous study of cumene used limited ozone; even in that study, the radical-induced decomposition amounted to only a small percent of the decomposition of the substrate.[3] (3) If the radical-induced decomposition were important, and since ring attack probably does not involve radicals whereas side-chain attack does,[2,3] then the ratio of ring to side-chain attack would vary as the reaction proceeds. In fact, this ratio remains constant. Similarly, since products protect the substrate against attack by radicals, the ratio of attack on two aromatic hydrocarbons would vary over the course of the reaction if radical-induced decomposition were important. However, as Table I shows, the relative rates of reaction of two aromatic hydrocarbons remain constant over the reaction course. (4) The selectivity we observe is not characteristic of either alkoxyl or peroxyl radicals. For example, with toluene taken as a relative *k* of unity, triphenylmethane[16] has a relative *k* of 9.6 for alkoxyl and 28 for peroxyl radicals (all per benzylic hydrogen), whereas toward ozone triphenylmethane gives a relative rate constant for total reaction of 4.1 (Table III) and a relative *k* for benzylic attack (per hydrogen) of 18.9 (Table IV).

When triphenylmethane is the substrate, reaction 2 gives a tertiary alkoxyl radical that can undergo β scission to form a carbonyl compound,[16] accounting for benzophenone as one of the products (eq 5). Benzophenone could also

$$Ph_3C\text{—}O\cdot \rightarrow Ph_2C{=}O + Ph\cdot \quad (5)$$

arise by a sequence of reactions involving the Wieland rearrangement of the tertiary alkoxyl radical[17] followed by

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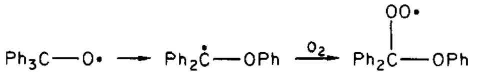
Table IV. Relative Benzylic Reactivity (per Hydrogen Atom) toward Ozone at 25 °C^a

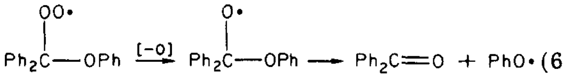
hydrocarbon	$k_{benzylic}$ (per hydrogen)	hydrocarbon	$k_{benzylic}$ (per hydrogen)
toluene (**1a**)	(1)	fluorene (**5a**)	10.3
diphenylmethane (**2a**)	3.32	triphenylmethane (**3a**)	18.9
ethylbenzene (**1b**)	3.88	9,10-dihydroanthracene (**4a**)	152
cumene (**1c**)	7.76	9,9-dimethyl-9,10-dihydroanthracene (**4b**)	165
9,10-dihydrophenanthrene (**6**)	8.5–9.6^a		

^{a}Based on estimated values for percent benzylic reactions, as discussed in the text and in Tables II and III.

reaction with ozone or oxygen and subsequent decomposition, eq 6a,b. A related decomposition to benzophenones



$$Ph_3C{-}O\cdot \longrightarrow Ph_2\dot{C}{-}OPh \xrightarrow{O_2} Ph_2\overset{OO\cdot}{C}{-}OPh \quad (6a)$$



$$Ph_2\overset{OO\cdot}{C}{-}OPh \xrightarrow{[-O]} Ph_2\overset{O\cdot}{C}{-}OPh \longrightarrow Ph_2C{=}O + PhO\cdot \quad (6b)$$

has been observed in the radical oxidations of triarylcarbinols by lead tetraacetate.[18] The occurrence of either eq 5 or 6 provides evidence that radicals are involved in these reactions, consistent with our earlier data.[2,3,19,20]

Table II summarizes the relative rate data obtained in the present study and also gives the values obtained by Nakagawa, Andrews, and Keefer, also at 25 °C.[5] The two sets of reactivities parallel each other, but Nakagawa et al. observed a slightly greater selectivity. While the differences between the two sets of data lie close to the experimental uncertainty, we feel that this selectivity difference is real and attribute it to the difference in solvents. The earlier workers used carbon tetrachloride whereas we used dichloromethane. We have observed a similar increase in selectivity for the ozonation of unsubstituted polycyclic aromatic hydrocarbons on changing to a less polar solvent.[21]

If one assumes that the electron-donating ability of the common alkyl groups are similar, then the rate of ring ozonation should be identical for all the monoalkylbenzenes we studied. If this is true, the increased reactivity of toluene, ethylbenzene, and cumene relative to *tert*-butylbenzene is equal to the different rates of hydrotrioxide formation. If it is assumed that *tert*-butylbenzene undergoes only ring ozonation, then the percent benzylic reactivity for a given alkylaromatic can be expressed as shown in eq II, where $k_{t\text{-Bu}}$ is the relative rate constant for

$$\%\ \text{benzylic reactivity} = 100(k_{tot} - k_{t\text{-Bu}})/k_{tot} \quad \text{(II)}$$

reaction of *tert*-butylbenzene.[22] The values for this quantity are shown in Table II. The value of 71% obtained for cumene by this method is in excellent agreement with the value of 72% obtained by spectroscopic analysis of the reaction mixture.[3]

The above approach can be extended to systems 2–6 that contain more than one aromatic unit. These compounds should have increased benzylic reactivity because of the greater delocalization for the benzylic intermediate formed. At the same time, the rate of ring ozonation increases for statistical reasons. (This increase actually is less than the statistical prediction since the electron-withdrawing effects of the aromatic groups on each other retard ring attack by an electrophilic species such as ozone.) Table III presents the total relative rate constants for ozonation of these compounds and the percent benzylic reactivity, determined by the above approach. That is, diphenylmethane (**2a**) was compared with 2,2-diphenylpropane (**2b**) (which was assumed to undergo only ring ozonation), triphenylmethane (**3a**) was compared with 1,1,1-triphenylethane (**3b**), etc. The total reactivity increases along the series toluene, diphenylmethane, and triphenylmethane, but the total relative rates are not directly proportional to the number of phenyl groups present (as would be expected if ring ozonation were the sole reaction occurring).

Certain formal derivatives of diphenylmethane, such as 9,10-dihydroanthracene (**4a**) and 9,9-dimethyl-9,10-dihydroanthracene (**4b**), show much greater reactivities than the parent system. These latter two compounds differ structurally from diphenylmethane in having the two aromatic groups "tied back" by a bridging group to create central, nonaromatic rings. Compounds of this type commonly react faster than their nonbridged analogues. Thus, 9,9-dimethyl-9,10-dihydroanthracene is over 1000 times more acidic than diphenylmethane.[23] Similarly 9,10-dihydroanthracene is over 300 times more reactive than diphenylmethane toward hydrogen atom abstraction by the *o*-allylbenzyl radical at 160 °C,[24] and 70 times more reactive toward benzyl radical at 170 °C.[25] The situation for carbocation formation is similar: 9,10-dihydroanthracene reacts readily with triphenylmethyl perchlorate to transfer a hydride ion whereas diphenylmethane is unreactive under these conditions.[26] The traditional explanation for all these examples is that the dihydroanthracene systems are better able to assume conformations that maximize overlap between the aromatic rings and the developing p orbital at the reaction site.

9,10-Dihydrophenanthrene (**6**) resembles the dihydroanthracene systems in that the benzyl positions have been incorporated into a central, nonaromatic ring. Each secondary benzylic position, however, is adjacent to just one aromatic unit. Allowing for statistical factors, therefore, the total reactivity of **6** might be thought to resemble that of ethylbenzene; however we find the total reactivity to be twice this value. Unlike the molecules previously considered, this compound is a formal derivative of biphenyl. Biphenyl undegoes ring ozonation with a rate of 0.72 ± 0.01 relative to di-*tert*-butylbenzene, which is about a factor of 10 greater than benzene. The biphenyl unit in 9,10-

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[22] (a) Replacement of benzylic hydrogens by methyl groups should not provide a site for ozonation since Williamson and Cvetanovic[22b] have shown that benzene undergoes ozonation nearly 1000 times as readily as neopentane. (b) Williamson, D. G.; Cvetanovic, R. J. *J. Am. Chem. Soc.* **1970**, *92*, 2949.

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dihydrophenanthrene should be even more prone to ring ozonation than the parent system both because alkyl substituents are present and because the central ring constrains the biphenyl unit to greater coplanarity. (The dihedral angle between the two rings in biphenyl[27] is 45° while the corresponding value for 9,10-dihydrophenanthrene is calculated[28] to be 24°.) A biphenyl group also should have a greater stabilizing effect on an adjacent trigonal carbon atom. Thus, for example, 4-phenylbenzyl tosylate is estimated to solvolyze 17 times faster than benzyl tosylate.[29] With these factors in mind, a statistically corrected total reactivity for **6** twice that for ethylbenzene appears reasonable.

Fluorene (**5a**) also can be regarded as a derivative of biphenyl. Since it is completely planar, it represents an idealized system for ring ozonation. A comparison of relative rates of total reaction for fluorene and 9,9-dimethylfluorene (**5b**) clearly indicates that fluorene is the most prone of the systems examined to undergo ring ozonation. We will return to fluorene's reactivity below.

The Mechanism of Ozonation at the Benzylic Position. Table IV lists the relative reactivity per benzylic hydrogen for ozonation of all of the hydrocarbons we have studied. On the basis of thermochemical arguments, Nangia and Benson have proposed that hydrocarbon hydrotrioxide formation takes place by hydride ion abstraction, as shown in eq 7.[30]

$$\text{R–H} + \text{O}_3 \rightarrow [\text{R}^+ + {}^-\text{OOOH}] \rightarrow \text{ROOOH} \qquad (7)$$

The order of reactivity in Table IV, cumene > ethylbenzene > toluene, and triphenylmethane > diphenylmethane > toluene, while consistent with this mechanism, also would be expected if the reaction involves the abstraction of a hydrogen atom (eq 8).

$$\text{R–H} + \text{O}_3 \rightarrow [\text{R}\cdot + \cdot\text{OOOH}] \rightarrow \text{ROOOH} \qquad (8)$$

Fluorene, however, provides evidence favoring the ionic reaction, eq 7. The benzylic reactivity of this compound is only 3 times that of diphenylmethane and $^1/_{15}$ that of the 9,10-dihydroanthracene type compounds. This seems to us to be most reasonable if the Nangia–Benson ionic mechanism is assumed to be operative.

The difference between the reactivities of fluorene and 9,10-dihydroanthracene is not attributable to factors associated with the differing ring size in the nonaromatic ring. In fact, the ease of carbocation formation is appreciably greater in cyclopentyl over cyclohexyl derivatives, as observed in solvolysis data.[31] While somewhat attenuated, the same order is observed in reactions leading to the corresponding radicals. For example, methyl radicals abstract hydrogen atoms slightly more readily from cyclopentane than from cyclohexane.[32] The ratio of reactivities for these compounds is 1.2, and annelation of aromatic rings to the cycloalkanes does not change the order of reactivity. The relative ease of hydrogen atom abstraction between indan and tetralin in reaction with bromotrichloromethane is 1.02 ± 0.06.[33] Similar relative reactivity is found for the ozonation of indan and tetralin (1.12 ± 0.03).

Fluorene is unique among the hydrocarbons in this study, since reaction at the benzylic positions creates a nonalternant system. The uneven charge distribution in nonalternant systems produces relative reactivities in carbocationic and anionic species that are not proportional, unlike the situation with alternant hydrocarbons. Fluorene forms an unusually stable *carbanion*; e.g., fluorene is an unusually strong carbon acid with a pK_a value approximately 10 units stronger than diphenylmethane.[23] Fluorene also forms *radicals* somewhat more readily than expected: Hydrogen abstraction from fluorene by the benzyl radical occurs 8 times more readily than from diphenylmethane;[23] fluorene also is 14 times more reactive than diphenylmethane in radical reaction with bromotrichloromethane.[33] In contrast, derivatives of fluorene form *carbocations* less readily than do the corresponding derivatives of diphenylmethane.[32]

Thus, the fact that the relative rate of ozonation of fluorene is $^1/_{15}$ of that of 9,10-dihydroanthracene is consistent with the hydride ion abstraction mechanism reflected in eq 7 and not with the hydrogen atom abstraction shown in eq 8. Were the mechanism a radical one, fluorene would be expected to react faster than dihydroanthracene.

Conclusion

The nature of the trends reported above lead us to propose that simple alkylbenzenes and polyphenylmethanes exhibit appreciable reaction with ozone at those benzylic positions that possess one or more hydrogen atoms. Variation in relative rates of the reaction of ozone at the benzylic position is due to substituent groups that stabilize the intermediate by inductive and/or delocalization effects. The relatively slow rate of reaction of fluorene favors eq 7 rather than eq 8 as the initial reaction. The hydrotrioxides produced in eq 7 decompose by radical reactions, eq 2–4, as shown by the production of benzophenone from triphenylmethane.

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Registry No. **2a**, 101-81-5; **2b**, 778-22-3; **3a**, 519-73-3; **3b**, 5271-39-6; **4a**, 613-31-0; **4b**, 42332-94-5; **4c**, 24269-10-1; **5a**, 86-73-7; **5b**, 4569-45-3; **6**, 776-35-2; toluene, 108-88-3; ethylbenzene, 100-41-4; cumene, 98-82-8; *tert*-butylbenzene, 98-06-6; *p*-di-*tert*-butylbenzene, 1012-72-2.

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[28] Unanue, A.; Bothorel, P. *Bull. Soc. Chim. Fr.* **1966**, 1640. Although both **4** and **6** may be nonplanar, benzylic hydrogens equilibrate rapidly and we have treated all benzylic hydrogens as equally reactive.

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