previously[4] as were donors 3–5.[3]

Decompositions were carried out under conditions described in Table I, following peroxide decomposition by iodimetry. Reactions in the presence of **4** were too rapid for accurate measurement, while for **5**, an experiment in an NMR tube at –20 °C showed complete reaction in <1 min (no further change in spectra). Induction of methyl methacrylate polymerization was detected by diluting reaction mixtures with petroleum ether. A run in the presence of anisole gave an intermediate precipitate of polymer, but none was detected with donors 3–5.

Products were determined on reaction mixtures of 0.5 mmol $(C_3F_7CO_2)_2$ and 2.5 mmol of donor in 2 mL of Freon-113, which had been allowed to react to completion at 0 °C, C_3F_7COOH was determined by titration, and the other products were separated by TLC on silica gel, using 8:1 hexane–ether for elution. All systems gave a single, sharp band, which was identified as described below. NMR measurements were all carried out as described for **6** below.

3-(Perfluoropropyl)-4-methoxytoluene (6): ^{1}H NMR (CDCl₃) δ 7.13 (m, 3 H), 3.83 (s, 3 H), 2.21 (s, 3 H); ^{19}F NMR (CDCl₃, CFCl₃ reference) 80.88 (t, 3 F), 120.34 (m, 2 F), 109.03 ppm (m, 2 F); MS, 290 (M⁺) base peak 289 (–H), also 242, 171, 121 (C₃F₇). The ^{1}H NMR establishes ring rather than side-chain substitution and M⁺ 290 shows that CO_2 has been lost. Fragmentation peaks at 289 and 121 are consistent with the structure given, but the isomer assignment is arbitrary.

p-Methoxybenzyl Perfluorobutyrate (7). The presence of this material as a minor component of **6** above is inferred from a small NMR singlet at δ 5.20 (cf. **11** below) and a small MS peak at m/e 234. That it is not the side chain substituted isomer at **6** is further indicated since the NMR singlet shows no splitting by neighboring CF_2.

2-[(Perfluorobutyryl)oxy]-1,4-dimethoxybenzene (8): ^{1}H NMR δ 6.85–7.04 (m, 3 H), 3.87 (s, 3 H), 3.77 (s, 3 H); ^{19}F NMR 81.25 (t, 3 F), 118.15 (m, 2 F), 123.60 ppm (M, 2 F) MS, 306 (M⁺) base peak 123 (C₃F₇CO₂, CH₃), also 213 (C₃F₇CO₂), 169 (C₃F₇), 154 (C₃F₇CO₂, +H). Both NMR and MS are consistent with the

structure assigned, which also parallels that previously observed in reactions of substituted benzoyl peroxides.

2,5-Di-*tert*-butyl-3-[(perfluorobutyryl)oxy]-1,4-dimethoxybenzene (9): ^{1}H NMR δ 6.98 (s, 1 H), 3.83 (s, 3 H), 3.30 (s, 3 H), 1.38 (s, 9 H), 1.33 (s, 9 H); ^{19}F NMR 81.12 (t, 3 F), 111.91 (m, 2 F), 122.33 ppm (m, 2 F); MS, 462 (M⁺), base peak 235 (R_FCOOH – CH₃), also 391, 250, 193, 179. A very small peak at m/e 424 and the larger one at 193 corresponding to the base peak at 235 suggest the presence of a small amount of **10** (**9** less one *tert*-butyl group), analogous to the major product in benzoyl peroxide reactions.

4-Methyl-2,5-dimethoxybenzyl Perfluorobutyrate (11): ^{1}H NMR δ 7.20 (s, 1 H), 6.75 (s, 1 H), 5.30 (s, 2 H), 3.84 (s, 3 H), 3.78 (s, 3 H), 2.20 (3 H); ^{19}F NMR 81.16 (t, 3 F), 105.79 (m, 2 F), 124.00 ppm (m, 2 F); MS, 378 (M⁺), base peak 165 (R_FCO_2), 196, 151, 135. The NMR singlets at δ 5.30 (2 H) and 2.20 (3 H) establish side-chain substitution. M⁺ at 389 shows that the CO_2 function is still present, and the fragmentation pattern is consistent with the structure assigned, which again parallels the results of our benzoyl peroxide experiments.

CIDNP experiments were carried out as described in the text. The strongly emitting proton was assigned on the basis of the NMR spectrum of **11** given above.

Oxidation of Alkylbenzenes by S₂O₈²⁻–Cu^II in Acetic Acid and Acetonitrile

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Oxidation of a series of toluenes by $K_2S_2O_8$ or $(NH_4)_2S_2O_8$ + $Cu(OAc)_2$ in acetic acid or acetonitrile is little affected by added water or acetate and gives benzyl acetates or benzaldehydes, respectively, in good yields. Data are consistent with initial formation of aromatic radical cations, proton loss to give benzyl radicals, and oxidation to final products by Cu^II. Benzyl alcohols, but not acetates, are selectively oxidized, suggesting partial equilibration of radical cations, with rates of proton loss determining product distributions. Oxidation of cumene gives chiefly α-methylstyrene which is oxidized further to 2-phenylpropanal. Products from p-ethyltoluene and p-cymene indicate that, on a statistical basis, loss of secondary and tertiary protons is more rapid than loss of primary protons, contrary to some previous reports. These systems appear promising for studying fragmentation patterns of aromatic radical cations in general.

It is generally believed that the side-chain oxidation of alkyl aromatics by one-electron oxidants can occur by two quite different paths. One, long known, is by abstraction of a benzylic hydrogen, as in free-radical halogenation or autoxidation. The other, less well understood, involves intermediate formation and fragmentation of a radical cation, e.g., as in eq 1 for toluene. Such a path has been

products (1)
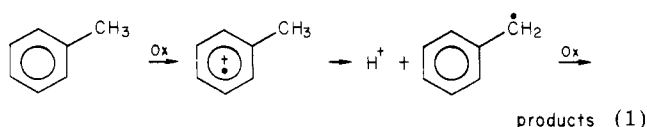
proposed for oxidation involving HO· and SO₄⁻·[3-6] with Co^III and other transition-metal ions[7] and also for anodic

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(3) Norman, R. O. C.; Storey, P. M. *J. Chem. Soc. B* **1970**, 1099.
(4) Snook, M. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 860.
(5) Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125.

Table I. Toluene-Peroxydisulfate
Oxidations in Acetic Acid

run	variations[a]	% conversion	% yield BzOAc[b]
1	NaOAc	67	92
2		56	63
3	NaOAc, H_2O	37	83
4	H_2O	46	76
5	H_2O, 10 min	48	68
6	H_2O, 4 h, 80 °C	39	84
7	NaOAc, N	69	78
8	N	54	81
9	N, 0.25 mmol Cu(Ac)$_2$	46	61
10	N, no Cu	45	25
11	N, 1 mmol CuSO$_4$	46	69

[a] Standard conditions: 2 mmol of $K_2S_2O_8$, toluene, 1 mmol of Cu(OAc)$_2$ in 5 mL of HOAc, 4 h at 120 °C. When present, NaOAc (4.5 mmol) and H_2O (1 mL) were used. N indicates (NH$_4$)$_2$S$_2$O$_8$. [b] Based on toluene consumed.

Table II. Toluene-$S_2O_8^{2-}$-Acetic Acid Material Balances

run	time, min	% conversion	% yield		
			BzOAc	BzOH	PhCHO
1-A[a]	20	50	62	5	30
1-B[a]	40	78	63	4	29
1-C[a]	100	80	66	3	29
2-A[b]	20	42	63	10	25
2-B[b]	40	72	67	11	21
2-C[b]	100	75	72	12	15
3[c]		78	67	5	25

[a] 2 mmol of toluene, 4 mmol of (NH$_4$)$_2$S$_2$O$_8$, 1 mmol of Cu(OAc)$_2$ in 5 mL of HOAc, 1 mL of H_2O at 120 °C. [b] Same plus 4.5 mmol of (NH$_4$)OAc. [c] Preparative run, 0.08 M toluene (see Experimental Section).

Table III. Toluene-$S_2O_8^{2-}$-Acetonitrile Oxidations[a]

run	time, h	% conversion[b]	% yield		
			PhCHO	BzOAc	BzOH
1[c]	2	20	70	17	7
2	0.5	25	72	1	20
3	3	26	76	2	17
4[d]	3	37	90	1	7
5[e]		36	78	3	10

[a] Standard conditions: toluene; (NH$_4$)$_2$S$_2$O$_8$, 2 mmol; Cu(OAc)$_2$, 1 mmol in 5 mL acetonitrile; 1 mL of H_2O, 100 °C. [b] Based on toluene reacted. [c] No H_2O. [d] 4 mmol of (NH$_4$)$_2$S$_2$O$_8$. [e] Preparative scale run, 0.08 M toluene (see Experimental Section).

oxidations.[8] Much of the work, including our own, has been in aqueous solution, which, from the point of view of synthetic utility, suffers from the drawback of low solubility of most organic substrates. On the other hand, few organic solvents (acetic acid and acetonitrile are exceptions) are sufficiently inert to be employed.

We have been interested in the pattern of side-chain fragmentation of radical cations as a function of reaction conditions and, in looking for a suitable experimental system, noted two rather contradictory reports on the oxidation of substituted toluenes by peroxydisulfate–Cu^{II} in acetic acid. Here the overall reaction is presumably a redox chain with propagating steps (eq 2–5). Jonsson and

$$HOAc + Cu(OAc) + S_2O_8^{2-} \rightarrow$$
$$SO_4^- \cdot + HSO_4^- + Cu(OAc)_2 \quad (5)$$
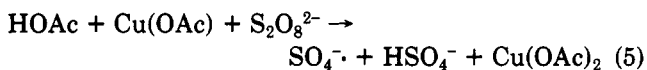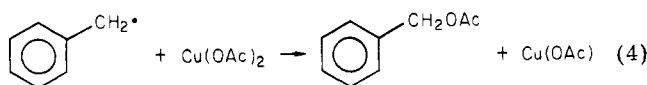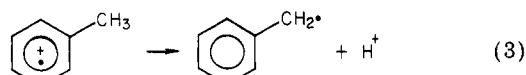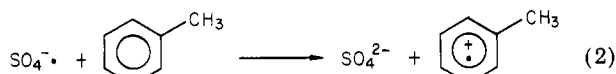
Wistrand[9] reported good yields of side-chain oxidation only in the presence of trifluoroacetic acid, which they suggested reduced the concentration of acetate ion which otherwise underwent competitive oxidation by $SO_4^- \cdot$. More recently, however, Belli, Giordano, and Citterio[10] have claimed that good yields are obtained in the presence of sodium acetate and describe their technique as a convenient synthesis of benzyl acetates.

In order to resolve the contradiction and to determine optimum conditions for the use of peroxydisulfate–Cu^{II} as a reagent for generating aromatic radical cations, we have

examined the oxidation of toluene and a number of related compounds in more detail, both in acetic acid and acetonitrile, and this paper reports our initial results.

Results and Discussion

Toluene Oxidations in Acetic Acid. The effect of reaction variables on the oxidation of toluene by K_2S_2-O_8–Cu(OAc)$_2$ was examined in a series of small-scale reactions (2 mmol each of toluene and peroxydisulfate in 5 mL acetic acid) in which consumption of toluene and formation of benzyl acetate was followed by quenching the reaction with water and GLC analysis of the organic layer after addition of internal standard. Table I shows typical results. Run 1 essentially duplicates the conditions of Belli et al. but indicates a higher potential yield than they report for isolated product. Ammonium peroxydisulfate may be substituted for the potassium salt, and Cu(OAc)$_2$ can be reduced or replaced by CuSO$_4$ (but not eliminated) with little effect on yield. Conversions and yields are also only slightly reduced by ommission of acetate or addition of a small amount of water. The requirement of 4 h of heating under Belli's conditions (run 1; shorter times give lower yields) is evidently due to the insolubility of $K_2S_2O_8$ in glacial acetic acid (extrapolation of literature data[12] indicate that, in water, the half-life of $S_2O_8^{2-}$ should be approximately 11 min). Use of more soluble (NH$_4$)$_2$S$_2$O$_8$ or addition of water gives much faster reaction (runs 3–6). Table II gives more detailed data on such partially aqueous systems, with 2 equiv of (NH$_4$)$_2$S$_2$O$_8$ in order to obtain higher conversions.

In these experiments acetate had little effect on conversion or yields, and reaction was complete within 1 h. Material balances for toluene are >95%, but about half the persulfate is consumed by oxidizing solvent or by some other path. The slightly lower yield of benzyl acetate observed here compared with those in glacial acetic acid

(6) Minisci, F.; Citterio, A.; Giordano, C. *Acc. Chem. Res.* **1983**, *16*, 27.
(7) Heiba, E. I.; Dessau, R. M.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 6830.
(8) Eberson, L.; Wistrand, L. G. *Acc. Chem. Res.* **1973**, *6*, 1777.
(9) Jonsson, L.; Wistrand, L. G. *J. Chem. Soc., Perkin Trans. 1* **1979**, 669.
(10) Belli, A.; Giordano, C.; Citterio, A. *Synthesis* **1980**, 477.
(11) This result is not surprising since peroxydisulfate is converted to bisulfate during reaction, and, in the absence of excess sodium acetate, the bisulfate reacts with copper acetate to yield copper sulfate in any case.

(12) Kolthoff, I. M.; Miller, I. K. *J. Am. Chem. Soc.* **1951**, *73*, 3055.

Table IV. Oxidation of Ring-Substituted Toluenes

substituent	condi-tions[a]	% con-version	% yield ArCH$_2$OAc[b]
p-OCH$_3$	A	79	71
	B	65	64
	C	60	41
	D	49	70[c]
p-Me	A	75	54
	B	63	43
	C	67	47
	D	21	71[d]
p-Cl	A	68	41
	B	48	37
	C	64	44
	D	33	70[e]

[a] A: toluene; K$_2$S$_2$O$_8$, 2 mmol; Cu(OAc)$_2$, 1 mmol; NaOAc, 4.5 mmol; HOAc, 5 mL; 4 h at 120 °C. B: as in A, except no NaOAc. C: as in B, but with (NH$_4$)$_2$S$_2$O$_8$ and 1 mL of H$_2$O for 30 min at 80 °C. D: toluene, 2 mmol; (NH$_4$)$_2$S$_2$O$_8$, 4 mmol; Cu(OAc)$_2$, 1 mmol in 5 mL of acetonitrile; 1 mL of H$_2$O; 3 h; 100 °C. [b] Based on toluene reacted. [c] Of ArCHO plus 4% ArCH$_2$OAc and 6% ArCH$_2$OH. [d] Of ArCHO plus 9% ArCH$_2$OAc and 9% ArCH$_2$OH. [e] Of ArCHO plus 6% ArCH$_2$OAc and 10% ArCH$_2$OH.

is evidently due to parallel formation of some benzyl alcohol which is rapidly oxidized further to benzaldehyde (see below). Run 3 shows that similar results are obtained on a 20 times larger preparative scale.

Since benzyl acetate is obtained in good yield under a variety of conditions, Jonsson and Wistrand's[9] conclusion that trifluoroacetic acid is required for efficient side-chain oxidation appears unfounded.

Toluene Oxidation in Other Solvents. Similar experiments were carried out in THF, *tert*-butyl alcohol, and acetonitrile, but only in acetonitrile were reactions of intrest clean enough to be observed. Results in acetonitrile (Table III) show that, while S$_2$O$_8^{2-}$ utilization is only about 50%, the reaction in 5:1 acetonitrile–water is rapid, gives a good material balance for toluene consumed, and gives up to a 90% yield of benzaldehyde as the principal product. Again run 5, using 20 times as much material, gives similar results on a preparative scale.

Oxidation of Substituted Toluenes. Experiments in both acetic acid and acetonitrile appear in Table IV. Those in acetic acid qualitatively confirm Belli's findings and again show little sensitivity to omission of sodium acetate or addition of a small amount of water. Runs in acetonitrile (conditions D) give substituted benzaldehydes in good yield, indicating that the reactions may have general synthetic promise for this purpose.

Since both conversions and yields vary with substituents, we have carried out some competitive oxidations of substituted toluenes to clarify the rate-determining steps which determine the variation (Table V). Although product distributions are similar for each toluene, the oxidation shows considerable selectivity towards toluenes with electron supplying groups. On the assumption that reactions are all first order in substrate, the data in acetic acid indicate relative reactivities of p-OCH$_3$/p-CH$_3$/p-Cl of 6.6:1.9:1 and 5.4:1.5:1 in acetonitrile.[13] On the assumption that benzaldehydes arise from further oxidation of benzyl alcohols, relative reactivities of benzyl alco-

hol/toluene can also be calculated from the date of Table V and of earlier tables where complete material balances are reported.[4] Results are not very accurate since benzyl alcohol yields are low but runs 2–4 in Table III give values for k (benzyl alcohol): k (toluene) of 19 ± 4 (standard deviation of the mean) in acetonitrile while Table II indicates slightly lower values in acetic acid: ~12 (run 1) and 7 (run 2 with added acetate). The experiments in Table V in acetonitrile indicate an increase in selectivity in the order p-OCH$_3$ < p-CH$_3$ < p-Cl (19, 67, and 112, respectively), and those in acetic acid show a similar trend.

Although the relative reactivities of substituted toluenes parallel relative rates of reaction of substituted benzoic acids with SO$_4^-$· as measured directly in water (3.5 × 10^9, 1.8 × 10^9, and 0.36 × 10^9 L mol^{-1} s^{-1} for p-OCH$_3$, p-CH$_3$, and p-Cl)[15] and are thus consistent with eq 2, SO$_4^-$· attack on substrate, being the rate-determining step in competitive oxidations, the high reactivities of benzyl alcohol compared with those of toluenes appears inconsistent with this. Since the alcohols contain an electronegative oxygen, this should, if anything, decrease the ease of formation of the resulting radical cation, and the implied reaction rates (10^{10}–10^{11} mol L^{-1} s^{-1}) are too high to be plausible. Two alternative explanations appear possible. Radical cations could be partially equilibrated by electron transfer, i.e., eq 6. Since proton loss from benzyl alcohol radical cations

$$A^+\cdot \ + \ B \ \rightleftharpoons \ A \ + \ B^+\cdot \qquad (6)$$
$$\downarrow \qquad\qquad\qquad \downarrow$$
$$products \qquad\qquad products$$
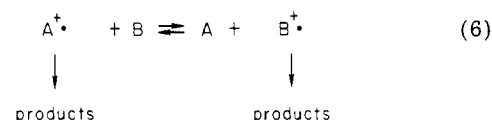
is apparently much faster than from toluene radical cations,[16] this would account for their selective oxidation. A similar suggestion has been made by Minisci to account for the selective oxidation of p-methoxytoluene in a mixture with the meta isomer.[6] Alternatively, in these nonaqueous media, Cu could be selectively solvated by the alcohols. As SO$_4^-$· was generated by reaction 5, it would be in immediate proximity to the benzyl alcohol and could react with it within the solvent cage. Such selective solvation of Fe in acetonitrile has been observed by Groves,[17] and there is evidence for such cage reactions in the Fenton's reagent oxidation of mandelic acid in water.[18,19]

Oxidation of Other Alkylbenzenes. Finally, we have carried out some preliminary experiments on the oxidation of benzenes with more complex alkyl side chains (Table VI). With ethylbenzene the results are straightforward and resemble those with toluene, except that now Cu oxidation of the intermediate benzylic radical yields some styrene, a well recognized path in the oxidation of radicals with β-hydrogen in these media.[20]

With isopropylbenzene, conversion to α-methylstyrene is evidently the major reaction path since it is the major product in reactions run for shorter times. Acetophenone and 2-phenylpropanal evidently come from its further oxidation, since they are obtained in high yield from ox-

(13) Calculated by the usual relation (ln A/A_0)/(ln B/B_0) = k_a/k_b.

(14) Here the kinetic scheme involves A $\xrightarrow{k_1}$ B $\xrightarrow{k_2}$ C and A $\xrightarrow{k_3}$ D, where D represents benzyl acetate and other unidentified products. The system can be treated exactly, but if $k_2/k_1 > 5$, it is well approximated (within 10%) by the steady-state assumption, giving k_2/k_1 = [A]/[B], regardless of how much A actually goes to D.

(15) Neta, P.; Madhavan, V.; Zemel, H.; Fessenden, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 163.

(16) The differences in rate in water have been estimated as over 10^3: Walling C.; Camaioni, D. M.; Kim, S. S. *J. Am. Chem. Soc.* **1978**, *100*, 4814.

(17) Groves, J. T.; Van Der Puy, M. *J. Am. Chem. Soc.* **1976**, *98*, 5290.

(18) Walling, C.; Amarnath, K.; Campbell, C. B. *J. Am. Chem. Soc.* **1982**, *104*, 1185.

(19) A third possibility, concerted oxidation and proton loss in benzylic alcohols, has been suggested in water[4] but now seems unlikely.[16] In any case, it can hardly account for the implausibly high rates for the SO$_4^-$·-alcohol rates required by the data.

(20) Kochi, J. K.; Bemis, A.; Jenkins, C. L. *J. Am. Chem. Soc.* **1968**, *90*, 4038, 4616.

Table V. Competitive Oxidations

run	toluene substituent	% conversion	% yield^c		
			ArCHO	ArCH$_2$OAc	ArCH$_2$OH
A^a	p-OCH$_3$	50	16	70	5
	p-CH$_3$	18	17	76	4
	p-Cl	10	14	80	trace
B^b	p-OCH$_3$	40	67	4	8
	p-CH$_3$	13	67	5	10
	p-Cl	9	73	4	9

^{a} 2 mmol of each toluene, 4 mmol of (NH$_4$)$_2$S$_2$O$_8$, 1 mmol of Cu(OAc)$_2$ in 5 mL of HOAc, and 1 mL of H$_2$O, at 120 °C for 3 h. ^{b} Same as in a but in 5 mL of acetonitrile and 1 mL of H$_2$O at 100 °C for 3 h. ^{c} Based on toluene consumed.

Table VI. Oxidation of Alkylbenzenes

substrate	conditions^a	% conversion	products	% yield^{b,c}
ethylbenzene	HOAc	62	1-phenylethyl acetate	60
			acetophenone	33
			1-phenylethanol	5
ethylbenzene	acetonitrile	95	acetophenone	88
			1-phenylethanol	5
			styrene	7
cumene	HOAc	33	α-methylstyrene	21
			acetophenone	25
			2-phenylpropanal	47
			1-phenylethyl acetate	3.6
			cumyl alcohol	3.6
cumene	acetonitrile	22	α-methylstyrene	69
			acetophenone	21
			2-phenylpropanal	10
			1-phenylethyl acetate	tr
			cumyl alcohol	tr
p-ethyltoluene	HOAc	66	p-methylstyrene	13 (10)
			1-p-tolylethanol	0.8 (27)
			p-ethylbenzaldehyde	8.3 (2)
			p-methylacetophenone	43 (36)
			p-ethylbenzyl acetate	35 (24)
p-ethyltoluene	acetonitrile	24 (28)	p-methylstyrene	22 (37)
			1-p-tolylethanol	3 (1) ·
			p-ethylbenzaldehyde	21 (6)
			p-methylacetophenone	52 (26)
			p-ethylbenzyl acetate	3 (31)
p-cymene	HOAc	61	p,α-dimethylstyrene	1.5
			2-p-tolylpropanal	23
			p-isopropylbenzaldehyde	12
			p-methylacetophenone	9
			p-isopropylbenzyl acetate	54
p-cymene	acetonitrile	12	p,α-dimethylstyrene	26
			2-p-tolylpropanal	4
			p-isopropylbenzaldehyde	39
			p-methylacetophenone	32
			p-isopropylbenzyl acetate	tr

^{a} 2 mmol of substrate, 4 mmol of (NH$_4$)$_2$S$_2$O$_8$, 1 mmol of Cu(OAc)$_2$ in 5 mL of solvent, and 1 mL of H$_2$O at 100 °C. ^{b} Based on substrate reacted. ^{c} Numbers in parentheses are for reactions with 4.5 mmol of NaOAc added.

idation of α-methylstyrene itself.[21] Again, this seems to be a case in which the initial product, α-methylstyrene, is oxidized more rapidly than the starting material, cumene, by a factor of 5–10 if we treat the data in the same way as those for the benzyl alcohol–toluene system.

Finally, oxidation of p-ethyltoluene and p-cymene yield products indicating competing loss of protons from both alkyl groups of the intermediate radical cation. There has been an impression that oxidation of methyl occurs preferentially or exclusively;[6,22,23] for example, p-isopropylbenzyl acetate has been reported as the sole isolated product (70%) from p-cymene oxidation by S$_2$O$_8$$^{2-}$-Cu in acetic acid.[22] However, under our conditions this is clearly

not the case. From the data, corrected statistically for the number of protons available, the ease of loss of primary/secondary/tertiary protons is about 1:2:1.6 in acetic acid. In acetonitrile the selectivity is greater, 1:4.8:4.8. On the basis of radical stability, an order of primary < secondary < tertiary might be expected, and the numbers may indicate some steric hinderance in the tertiary case.

Summary

(1) Our results confirm that S$_2$O$_8$$^{2-}$-Cu^{II} oxidation in acetic acid and acetonitrile is a promising technique for generating aromatic radical cations and studying their subsequent reactions. Although some S$_2$O$_8$$^{2-}$ is lost by oxidation of solvent, identifiable products are obtained in high yield based on substrate consumed.

(2) Not only are toluenes converted to benzyl acetates in acetic acid as previously reported but also the reaction in acetonitrile gives benzaldheydes in high yield, so both reactions appear synthetically useful.

(21) This interesting reaction is being examined further and will be reported elsewhere.

(22) Onopchenko, A.; Schulz, J. G. D.; Seekircher, R. *J. Org. Chem.* **1972**, *37*, 1414, 2564.

(23) Giordiano, C.; Belli, A.; Citterio, A.; Minisci, F. *J. Org. Chem.* **1979**, *44*, 2314–5.

(3) Ethylbenzene and cumene are also readily oxidized, cumene giving initially principally α-methylstyrene which is rapidly further oxidized to 2-phenylpropanal and acetophenone.

(4) *p*-Ethyltoluene and *p*-cymene undergo competitive oxidation of both alkyl groups with a 2–4:1 preference for proton loss from the more substituted benzylic carbon.

(5) In competitive oxidations, toluenes with electron-supplying groups are attacked preferentially. Similarly, benzyl alcohols and styrenes are oxidized in preference to their parent alkylbenzenes. Here the large spread in reactivity is inconsistent with known or expected rates of $SO_4^-\cdot$ reactions with these substrates and may arise from electron transfer between radical cations and substrates, with the result that relative rates of side-chain cleavage become important in determining apparent relative substrate reactivities. In fact, the variation in product distributions under different conditions which we find and discrepancies between our findings and those in the literature imply that radical cation fragmentations are quite complex and will reward further study.

Experimental Section

Reagents and solvents were commercial materials, and purity checks were by GLC or other appropriate means.

Reactions were in general carried out in sealed 15-mL Teflon-capped vials flushed with argon or nitrogen and magnetically stirred in thermostated baths as indicated in the tables. In runs where only major products were determined, reaction mixtures were analyzed directly by GLC against internal standards (Carbowax OV-17 column) and comparison with authentic material.

When complex mixtures of products were obtained, e.g., Table VI, reaction mixtures were poured into water, extracted with ether, dried, and, after removal of ether, analyzed by a combination of GLC and GC/MS (VG Micromass 7070 mass spectrometer) with comparison with reference spectra when available. Thus 2-phenylpropanal [M+·, m/e 134; base peak, m/e 105 (M – CHO)] matched the reference spectra for authentic material, and 2-*p*-tolylpropanal (M+·, m/e 148, base peak, m/e 119 (M – CHO); also m/e 91 ($C_7H_7^+$), and a general fragmentation pattern similar to 2-phenylpropanal above] was clearly distinguished from *p*-isopropylbenzaldehyde [M+·, m/e 148; base peak, m/e 133 (M – CH₃); also m/e 119 (M – CHO) and 105 (M – C_3H_7)].

# Oxidation of Arylalkanols by $S_2O_8^{2-}$–CuII

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Products of oxidation of a series of arylalkanols by $S_2O_8^{2-}$–CuII in acetic acid and acetonitrile are consistent with initial oxidation to aryl radical cations followed by either loss of a benzylic proton or C–C bond scission and subsequent oxidation of intermediate benzylic radicals by CuII to final products. 1-Arylalkanols (ArCHOHR) react by both paths, C–C bond scission increasing with stability of the radical R·. 2-Arylalkanols (ArCH₂CHOHR) give chiefly C–C bond scission to benzyl radicals and RCHO. The 3- and 4-arylalkanols undergo chiefly proton loss, and the resulting radicals are oxidized with cyclization to chromans and 2-phenylfurans, respectively, both of which may be oxidized in turn to further products.

It is generally accepted that side-chain oxidations of aromatic molecules by higher valence metals and other reagents which may act as one-electron oxidants often involve initial oxidation of the aromatic to a radical cation.[3-6] The radical cation then undergoes loss of a benzylic proton or the side-chain fragmentation, and the resulting radicals are further oxidized to final products. The use of peroxydisulfate plus Cu(II) to oxidize intermediate radicals is a convenient technique for studying such reactions, and we have recently described the effect of reaction variables in the oxidation of toluenes and some other alkylbenzenes in acetic acid and acetonitrile.[7] Of particular interest are molecules where competing paths of fragmentation are available. Here an interesting example

Scheme I

(A)

(B)
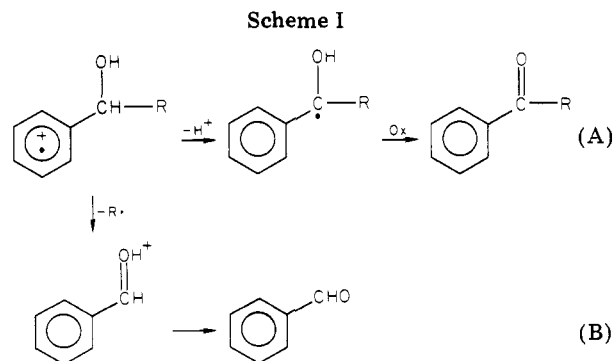
has been reported by Snook and Hamilton,[4] who found that $S_2O_8^{2-}$ oxidation of arylalkyl carbinols (ArCHOHR) in aqueous solution occurs by two paths involving the competing cleavages (Scheme I).

As might be expected, path B was favored by increasing the stability of the radical R· in the order Me < Et < *i*-Pr < *t*-Bu. We have now examined the competition in acetic acid and acetonitrile and find that the competition is also

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