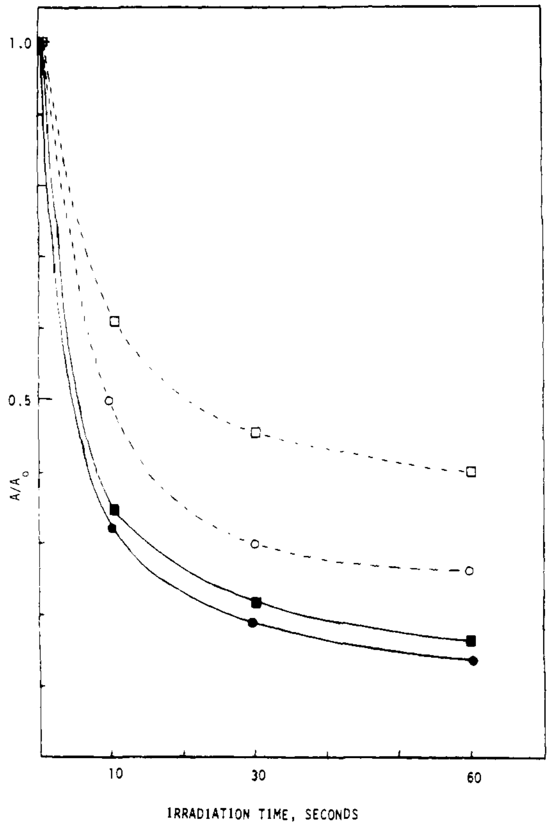

Figure 1. Plot of A/A_0 vs. irradiation time for monolayer assemblies of **1** with TP and arachidic acid: [●] six adjacent layers of **1**:TP in a 1:4 ratio; [■] six adjacent layers of **1**:TP, 1:4; [○] six layers of **1**:TP, 1:4 alternating with layers of pure TP; [□] six layers of **1**:TP, 1:8 alternating with layers of pure TP.

tivity of both **1** and **2** is comparable in the assemblies. Irradiation of assemblies incorporating **1** or **2** at 366 nm results in a decrease in the long-wavelength absorption band and fluorescence and a concomitant increase in absorption at 265 nm. By analogy to the solid state photochemistry of **1**, we infer that the photoproduct in the assemblies is a dimer.[11] This is consistent with the observation that the rate and extent of disappearance of **1** decreases at higher TP:**1** ratios. In addition, the efficiency is decreased when layers containing **1** are alternated with layers of pure TP, implying that both intra- and interlayer dimerization are important (Figure 1).

In both the solid state and in the monolayer assemblies a red-shifted (green) fluorescence is present in those systems where photodimerization takes place; the fluorescence declines in intensity as the dimer builds up. In the monolayer assemblies residual blue (apparently monomer) fluorescence persists following the initial fast reaction. These observations suggest that the green fluorescence may be due to an excimer intermediate in the photodimerization. However, the possibility that the formation of the emissive "excimer" state[12] and dimerization are competitive rather than sequential processes cannot be excluded. In contrast to the above, no solution photodimerization or excimer emission could be observed in saturated solutions of **1** (ca. 0.008 *M*) in acetonitrile; since shorter chain 4-stilbazole salts photodimerize in solution,[13] the apparent effect of the long chains is to inhibit association in solution. Although a number of polar aromatic molecules and salts of heteroaromatics are known to photodimerize in the solid state,[6] the dimers formed are almost invariably of the head-to-tail structure analogous to **5**, reflecting perhaps a minimization of steric and like-charge repulsions. In fact 2-stilbazole methiodide photodimerizes quantitatively in the solid state to yield such a product.[7,14] In contrast, the sole photodimer of **1** in the solid state has the head-to-head structure **4**; this result suggests that in the solid state preferential association of hydrophobic groups may be important enough to offset unfavorable like-charge interactions in the hydrophilic zones. This result suggests that incorporation of an orienting hydrophobic group could lead to useful directing effects on solid state photodimerization and addition reactions. We are currently exploring this possibility with several systems.

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(7) Irradiation of 4-stilbazole (1 g/100 ml) in 0.1 *M* HCl gave predominently (ca. 80%) the head-to-tail dimer corresponding to **5** as described by Abernethy.[8] In addition, a second dimer (ca. 10–15%), mp 196–196.5°, could be isolated. The dimer is assigned the structure analogous to **6** on the basis of its NMR spectrum (cyclobutane protons at δ 3.71) and the presence of a significant diazaphenanthrane peak (*m/e* 180.0711, 46%; calcd for $C_{12}H_8N_2$, 180.0687) in the mass spectrum.
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Aromatic Hydroxylation by Peroxydisulfate

Sir:

Although the oxidation and cleavage of aromatic side chains by peroxydisulfate (usually in the presence of transition metal ions) is well known,[1-3] as far as we are aware, the Elbs reaction (hydroxylation of phenols in alkaline medium) provides the only example in which hydroxyl groups are efficiently introduced into the aromatic ring.[4] Oxidation of aromatics by Fenton's reagent (Fe^{2+}–H_2O_2) has also been reported to give solely side-chain oxidation of a number of aromatics,[2,3] but recently we have found that phenols

Table I. Aromatic Hydroxylation by Fe^{2+}–$S_2O_8^{2-}$ Reagent[a]

Substrate	Products (%) Phenolic	Products (%) Other
Benzene	64	< 1 Biphenyl
Toluene	21 (62–5–33)[b]	15 Benzyl alcohol
β-Phenylethanol	40 (51–12–37)[b]	27 Benzyl alcohol 3 Styrene glycol
Phenylacetic acid	20 (39–18–43)[b]	47 Benzyl alcohol

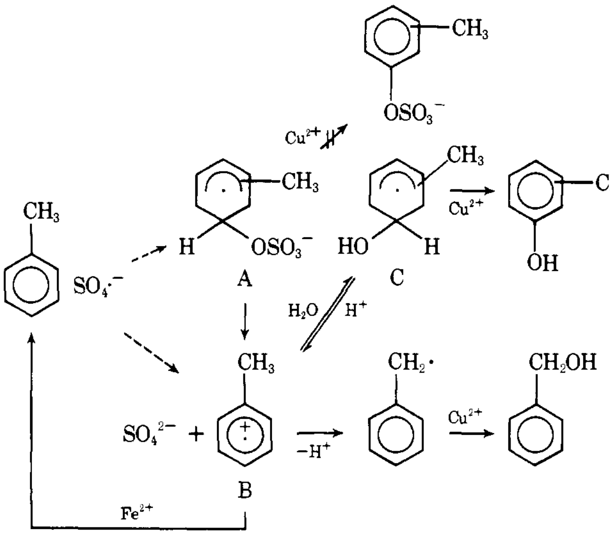
[a] All runs by slow addition of excess Fe^{2+} to systems $[S_2O_8^{2-}] \sim 8 \times 10^{-3}$ *M*, $[Cu^{2+}] = 0.24$ *M*, $[H^+] = 0.05$ *M*, substrate = 0.05–1 *M* (two-phase with benzene and toluene), $T = 30°$. Yields are based on $S_2O_8^{2-}$. [b] Ortho–meta–para ratios in phenolic products.

can be made the major products by carrying out the reaction in the presence of Cu^{2+} ion.[5] We here report that oxidation of a variety of aromatic molecules by $S_2O_8^{2-}$–Fe^{2+} in the presence of Cu^{2+} also gives phenolic products in good yield, a result which has important bearing on the path of reaction of both HO· and $SO_4\cdot^-$ radicals with aromatics, and which also may be of some synthetic interest.

Unless indicated, experiments were carried out by adding Fe^{2+} to $S_2O_8^{2-}$–Cu^{2+} substrate systems in dilute acid (with ClO_4^- as the counterion) and analyzing products by GLC, usually after silation. Typical results are shown in Table I, and, except for the case of phenylacetic acid, yields of phenolic products are quite comparable to those obtained with H_2O_2 under the same conditions.[5]

We believe our results are best rationalized by the following scheme using toluene as an example which has many features in common with that which we have proposed for the H_2O_2 system.[6]

$$S_2O_8^{2-} + Fe^{2+} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4\cdot^- \qquad (1)$$



(2)

Whether $SO_4\cdot$ radicals initially add to the aromatic ring, as has been proposed by Norman[2,7] (although he was unable to detect esr signals of hydroxycyclohexadienyl radicals and side chain cleavage products[7]), or directly oxidize the aromatic to the radical cation[3] is not determined,[8] but the formation of phenols clearly shows that initial side-chain attack is usually of minor importance.

A second conclusion is that our results are further evidence for the very fast reversible hydration of the intermediate radical cation B, which seems to us the most plausible way of accounting for the formation of phenolic products. The possibility that an initial adduct A is oxidized to an aryl sulfate which subsequently hydrolyzes is ruled out, because hydrolysis is very slow in cold dilute acid.[9] With benzene we have shown that no appreciable phenyl sulfate ion is present in our reaction mixtures, since no increase in phenol yields occurs when they are heated for prolonged periods. A second possibility, that hydroxyl radicals are formed via the exchange

$$SO_4\cdot^- + H_2O \longrightarrow HSO_4^- + HO\cdot \qquad (3)$$

and then add to yield C directly is unacceptable, because it is now clear that eq 3 is very slow except in alkaline solution.[10] A third alternative, some direct oxidation of B, cannot be unequivocally excluded but seems an unnecessary hypothesis in view of Norman's observation of species C in these systems and our earlier results with H_2O_2 oxidations.[5]

Table II. Benzene Hydroxylations

Conditions[a]	Yield (%) Phenol	Yield (%) Other
Fe^{2+}, no Cu^{2+}	26	24 Biphenyl
Fe^{2+}, Cu^{2+}	64	
Thermal (75°)	10	3 Biphenyl
Thermal + Cu^{2+} (60°)	54	
Ag^+, 10^{-3} *M* (40°)	3	Polymers
Ag^+, Cu^{2+} (40°)	43	Polymers

[a] Conditions similar to those in Table I.

In contrast to the other substrates, phenylacetic acid gives significantly less phenolic products than are obtained with H_2O_2 (55% under the same conditions). $SO_4\cdot^-$ radicals are known to decarboxylate aliphatic acids,[7] and it may be that here side-chain attack on the carboxyl group, as proposed by Tanner[11] competes with oxidation of the aromatic ring. Recent results by Minisci indicate that this competition varies with experimental conditions: oxidation of γ-phenylbutyric acid by $S_2O_8^{2-}$ alone gives predominantly phenyl butyrolactone, but chiefly decarboxylation with Ag^+ or at higher pH's.[12]

Peroxydisulfate can also be decomposed to $SO_4\cdot^-$ radicals either thermally or by traces of Ag^+. Table II shows that in the presence of Cu^{2+}, these techniques also convert benzene to phenol in good yield but give little or no identifiable product in its absence.

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