sponding to IX and X. Treatment of this mixture with excess base gave II, while alcoholic hydrogen chloride furnished the indole III. The originally puzzling results discussed in the first paragraph can now be explained by the rapid formation (confirmed by thin layer chromatography) of the enolate anion corresponding to IX, *via* benzoyl and proton transfer. In the absence of additional sodium methoxide, this anion remains in the mixture until work-up, acidification then producing III. With excess base, however, irreversible ring closure to oxindole occurs *via* the dianion of the enol. The mechanism will be discussed more thoroughly in the full paper.

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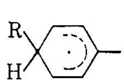
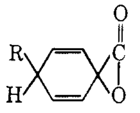
Behavior of a σ Radical with a Peroxide Functional Group

Sir:

Radical-substituted peroxides are of interest in connection with the problem of radical-induced decomposition of peroxides. Attack of radicals on the ring of an aroyl peroxide can give rise to species **1**, **2**, or **3**. Species **1** and/or **2** are believed to be intermediates for induced decomposition.[1] Our results indicate that species **3** does *not* lead to induced decomposition.


1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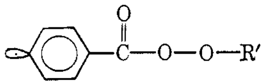
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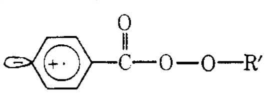
Experiment[2,3] and simple molecular orbital considerations agree that the unpaired electron in the ground state of phenyl radicals occupies a carbon sp^2 σ orbital, with very little unpaired spin density in the π system. The isomerization of **3** to structures such as **4**–**6** might require a considerable activation energy, although no accurate theoretical prediction can be made at this time.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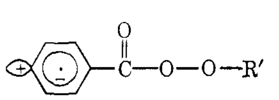
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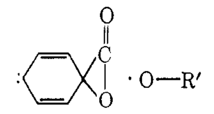
6

We have generated **3** (R′ = *p*-iodobenzoyl) by decomposing bis(*p*-iodobenzoyl) peroxide[4] in degassed carbon tetrachloride at 79.8°. The disappearance of peroxide titer is precisely first order, with $k = 1.84 \times 10^{-5}$ ($\pm 4\%$) sec^{-1}. The products are *p*-diiodobenzene, *p*-dichlorobenzene, *p*-chloroiodobenzene, carbon dioxide, and hexachloroethane, accounting for 100% of the peroxide and excluding the possibility of a first-order, induced-decomposition process.[5] Within experimental error, the yields of *p*-diiodo- and *p*-dichlorobenzenes are equivalent, but are dependent on the initial concentration of peroxide, as shown in Table I.

Table I. Aromatic Products of Decomposition of Bis(*p*-iodobenzoyl) Peroxide in Carbon Tetrachloride

Initial concn of Peroxide, $M \times 10^2$	Moles/mole of peroxide		
	p-IPhI	*p*-ClPhCl	*p*-ClPhI
1.59	0.14	0.15	1.70
8.02	0.50	0.41	1.21

p-Diiodobenzene can come from *p*-iodophenyl radical attack either on the peroxide itself (leading to **3**) or on *p*-chloroiodobenzene.[6,7] However, upon work-up of the peroxide after about 15% decomposition[8] the *p*-iodo substituents *in the undecomposed peroxide* were found to have been replaced by *p*-chloro substituents to an extent equivalent to ~42% of the peroxide decomposed. It should be noted that the substituent effects of *p*-chloro and *p*-iodo on the unimolecular decomposition of benzoyl peroxide are expected to be indistinguishable.[4,5]

We conclude, therefore, that the *para*-σ radical substituted peroxide is formed without concerted decomposition of the peroxide, and that it persists unchanged long enough to abstract chlorine from solvent, about 10^{-6} to 10^{-7} sec.[9]

Acknowledgment. We wish to acknowledge support of this work by the Army Office of Research, Durham, N. C., and by the National Institutes of Health.

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Catalysis of Ionic Reactions by Polyelectrolytes. Reaction of $Co(NH_3)_5Cl^{2+}$ with Hg^{2+} in Polysulfonic Acid Solutions[1]

Sir:

In previous communications from this laboratory[2–4] it was suggested that a polyion should catalyze strongly any reaction involving two counterions. Furthermore, this catalytic effect could be used to study the distribu-

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