tected by the isotope effect technique. Preliminary results demonstrate substantial deuterium isotope effects in the bromination of 4-methyl[2.2]paracyclophane.[8]

[8] The authors wish to thank the National Science Foundation for a grant used in support of this research. H. J. R. also wishes to acknowledge a U. S. Rubber Co. tuition grant for 1967.

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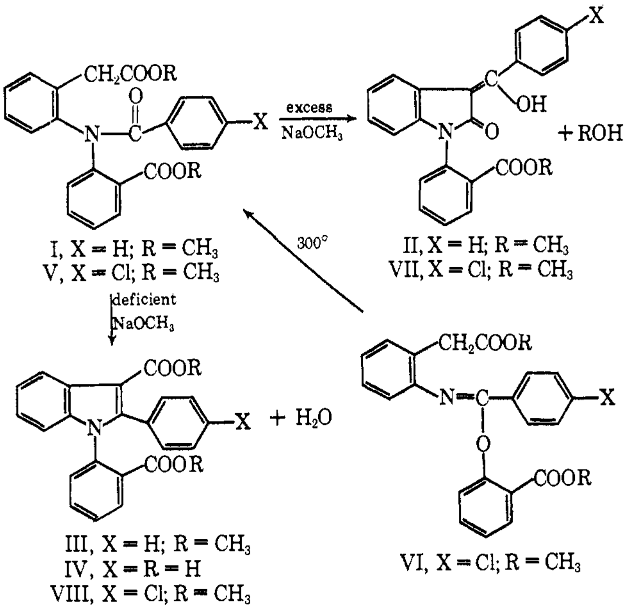
## Isolation of Crystalline Keto–Enol Tautomers. Conversion into Indoles and Oxindoles

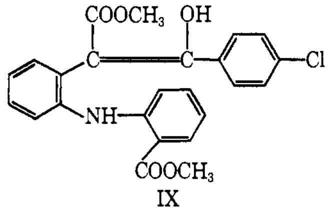
*Sir:*

Several years ago we reported that treating the N-benzoyldiphenylamine diester I with excess sodium methoxide in benzene failed to give the expected Dieckmann product but instead furnished the oxindole II.[1] It has now been found that use of slightly less than 1 equiv of the same base, followed by acidification with hydrochloric acid, afforded little or no II but gave instead the indole diester III in 63% yield.[2]

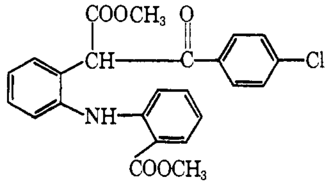


The structure of III, mp 140–144°, was determined by elemental analyses[3] and spectra;[4] the ultraviolet spectrum ($\lambda_{max}$ 235 m$\mu$ ($\epsilon$ 36,200) and 294 (19,600)) was indicative of the indole nucleus while infrared bands at 5.79 and 5.87 $\mu$ and nmr peaks at $\delta$ 3.75 and 3.43 showed the presence of two carbomethoxy groups.[5] Hydrolysis of III with excess potassium hydroxide in aqueous methanol gave the dibasic acid IV, 85%, mp 215–218° dec, while treatment with 1 equiv of sodium methoxide gave 23% of half-ester acid, mp 259–266°, identical with material previously obtained as a by-product in the synthesis of II.[1]

The *p*-chloro analog V, mp 109–111°, was prepared in 85% yield by Chapman rearrangement[1,6] of the imidate VI, mp 96.5–99°. Reaction of V with excess sodium methoxide in benzene gave the yellow oxindole VII, 71%, mp 179–183°, positive $FeCl_3$ reaction, $\delta$ 12.4 (enolic proton) and 3.63 ($OCH_3$). On the other hand, when the reaction was carried out with a slight deficiency of base,[2] the major product (54%) was neither the oxindole VII nor the indole VIII, but instead an isomer of V shown to be the enol IX, white prisms, mp 110–122° (variable), positive $FeCl_3$ reaction, $\delta$ 13.5 (enol OH), 9.33 (NH), and 3.80 and 3.70 (sharp singlets for the two carbomethoxy groups).



IX



X

Recrystallization of the enol from methanol gave two types of prisms which were hand picked. The minor fraction was then used to seed a solution obtained by refluxing the enol in methanol for 1 hr. Slow crystallization resulted, furnishing the keto compound X as pale yellow prisms, mp 93–99°, 68%, negative $FeCl_3$ reaction, $\delta$ 9.38 (NH), 5.75 (singlet, CHC=O), and 3.88 and 3.72 ($OCH_3$). Treatment of either enol IX or keto X with excess sodium methoxide in benzene afforded oxindole VII while the reaction of either isomer with trifluoroacetic acid in chloroform furnished the white indole VIII, mp 194–197.5°, negative $FeCl_3$ reaction, $\delta$ 3.78 and 3.45. Both IX and X reacted at once with bromine in carbon tetrachloride, but in each case the isolated product was the indole VIII.

The marked differences in the nmr spectra of IX and X, both with respect to the enolic H and one of the $OCH_3$ groups, facilitated the analysis of mixtures.[5] Solutions of either compound in deuteriochloroform were essentially unchanged after 24 hr at room temperature, but addition of one drop of triethylamine to either solution furnished the equilibrium mixture containing 30% enol. Refluxing methanol solutions of IX or X for 4 hr led to the same 3:7 ratio, but in boiling hexane (24 hr) the keto form (55%) predominated. When IX or X was heated without solvent, the mixture contained ~25% enol, but equilibration was still incomplete after 3 hr at 100°. At 125° a complex mixture of VII, VIII, IX, and X resulted.

The reaction of the parent compound I with a deficient amount of base was then explored further. *Careful* acidification of the reaction mixture led to a gum which was shown by nmr ($\delta$ 13.5 and 5.78) to contain both the enol and keto compounds corre-

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(1) J. W. Schulenberg and S. Archer, *J. Am. Chem. Soc.*, **83**, 3091 (1961).

(2) Use of an old bottle of commercial sodium methoxide, which was later found to have a base content of only 80%, led to the serendipitous result.

(3) Satisfactory analyses were obtained for new compounds.

(4) Ultraviolet spectra were run in 95% ethanol, infrared spectra in potassium bromide, and nmr spectra in deuteriochloroform (internal TMS).

(5) I wish to thank Dr. R. K. Kullnig and Miss C. M. Martini for spectral interpretations which were instrumental in establishing the structures of new compounds and the composition of mixtures.

(6) J. W. Schulenberg and S. Archer, *Org. Reactions*, **14**, 1 (1965).

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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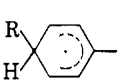
## Behavior of a $\sigma$ Radical with a Peroxide Functional Group

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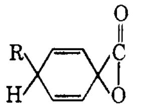
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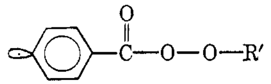
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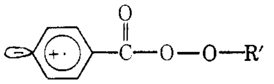
Experiment[2,3] and simple molecular orbital considerations agree that the unpaired electron in the ground state of phenyl radicals occupies a carbon sp$^2$ $\sigma$ orbital, with very little unpaired spin density in the $\pi$ system. The isomerization of **3** to structures such as **4–6** might require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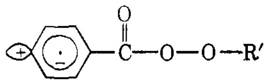
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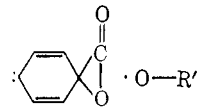
6

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<br>*p*-IPhI | <br>*p*-ClPhCl | <br>*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-$\sigma$* 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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(1) C. Walling and E. S. Savas, *J. Am. Chem. Soc.*, **82**, 1738 (1960); C. Walling, Abstracts, 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1967, No. 131; C. Walling and Z. Čeković, *J. Am. Chem. Soc.*, **89**, 6681 (1967).

(2) G. Porter and B. Ward, *Proc. Roy. Soc.* (London), **A287**, 457 (1965).

(3) J. E. Bennett, B. Mile, and A. Thomas, *Chem. Commun.*, 265 (1965).

(4) W. Cooper, *J. Chem. Soc.*, 3106 (1951).

(5) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, 72, 5426 (1950).

(6) J. F. Bunnett and C. C. Wamser, *ibid.*, **88**, 5534 (1966).

(7) D. L. Brydon and J. I. G. Cadogan, *Chem. Commun.*, 744 (1966).

(8) Reduction of the undecomposed peroxide with NaI–acetone, followed by acidification, yielded the acids. Treatment of the acids with diazomethane–ether yielded methyl esters, which were separated by vapor phase chromatography.

(9) W. H. Starnes, Jr., *J. Org. Chem.*, 31, 1436 (1966).

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## Catalysis of Ionic Reactions by Polyelectrolytes. Reaction of Co(NH$_3$)$_5$Cl$^{2+}$ 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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(1) This work was supported by Grant GM-05811 of the National Institute of Health. One of us (B. V.) is indebted to the Institute of General Medical Sciences of the National Institutes of Health for a predoctoral fellowship, No. GM-28628.

(2) H. Morawetz and E. W. Westhead, Jr., *J. Polymer Sci.*, **16**, 273 (1955).

(3) H. Morawetz, *ibid.*, **42**, 125 (1960).

(4) H. Morawetz and J. A. Shafer, *J. Phys. Chem.*, **67**, 1293 (1963).