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Ipso-substitution Reactions of 3-Substituted Indoles with Benzoyl t-Butyl Nitroxide

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Summary Reactions between benzoyl t-butyl nitroxide and certain 2-phenylindoles carrying a substituent at C-3 give 2-phenyl-3H-indol-3-one; 2-phenylindole itself gives compound (7).

DURING the past decade several examples of free-radical ipso-substitution reactions in various substituted aromatic compounds have been described.¹ We now report examples of ipso-substitution by an acyl nitroxide.

Benzoyl t-butyl nitroxide² (1) (representative of the isolable acyl tertiary-alkyl nitroxides, which are excellent selective oxidising agents for a wide variety of organic substrates³) was allowed to react in benzene with a series of 3-substituted 2-phenylindoles (2). Major products isolated in each case were the indolone (5), N-t-butylbenzamide (6), and the hydroxamic acid (4). The reactions were carried out using indole to nitroxide ratios of $1:2\cdot2$. The indolone partially decomposed during chromatographic isolation, and its yield from each indole was therefore determined by h.p.l.c. (Table).

TABLE.Formation of 2-phenyl-3H-indol-3-one (5) from 3-sub-
stituted 2-phenylindoles (2) in benzene.

Substituent X	Yield/%	T∕°C	t/h
N=NPh	80	25	24
CH2OH	70	"	**
CI -	25	"	"
N=NC ₆ H ₄ NO ₂ -p	70	Reflux	2
SMe	20	**	"
SCN	20	**	**

A reaction sequence which partially accomodates the formation of the identified products is outlined in the Scheme. The initial step is consistent with the fact that



SCHEME

the N-methyl derivative of (2) did not react with the nitroxide. No other products were isolated, and the fates of the original 3-substituents are unknown.

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When compound (1) reacted with 2-phenylindole itself, (5) was apparently not formed; instead, a major product was compound (7), whose structure was confirmed by comparison with an authentic sample.⁴ This result has a precedent in the oxidation of 2-methylindole by Fremy's radical,⁵ but reaction of 2,3-disubstituted indoles with Fremy's radical has apparently not been investigated. It should, however, be noted that oxidation by Fremy's radical of phenols having a bromine or chlorine atom in the para position is accompanied by displacement of the halogen

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in the intermediate phenoxyl radical in a process similar to that outlined here.6

The variant of *ipso*-substitution which is exemplified by the present results, in which a radical derived from an aromatic substrate couples with a second radical species at the position which bears the substituent that is displaced, may account for some of the more surprising examples of free-radical ipso-substitution recorded in the literature.7

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