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MORE ON THE NITROSOACETANILIDE REACTION

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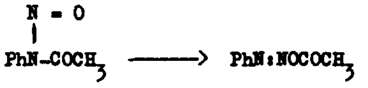
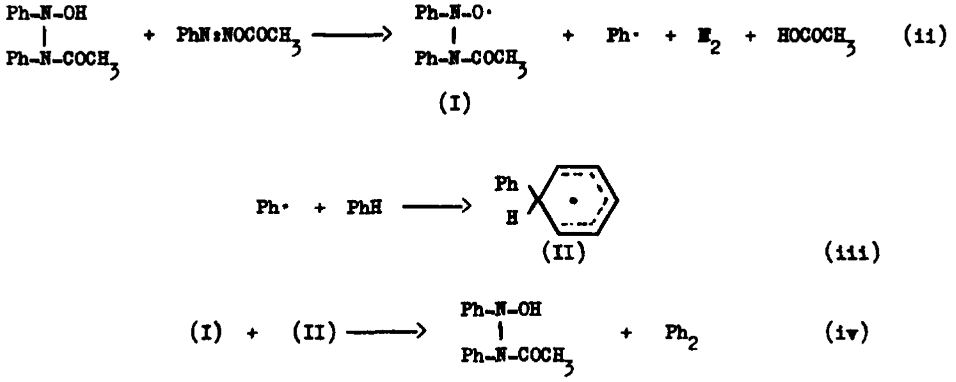
We recently demonstrated[1] that the stable radical which had been detected[2] during the thermal decomposition of N-nitrosoacetanilide in benzene has the structure (I), and this has been amply confirmed.[3]

An earlier structure proposed for the relatively stable radical detected in this reaction was $PhN{:}NO^{\cdot}$;[2] this formed the basis of an ingenious mechanistic interpretation[4] of the reaction which accounted for the high yields of acetic acid, and for the absence of high molecular weight hydrocarbons, among the reaction products. We suggested[1] a possible alternative scheme based on radical I, in which the key steps are:



$$PhN(N{=}O)\text{-}COCH_3 \longrightarrow PhN{:}NOCOCH_3 \qquad (i)$$

followed by the chain sequence:



$$Ph\text{-}N(OH)\text{-}N(COCH_3)\text{-}Ph + PhN{:}NOCOCH_3 \longrightarrow \underset{(I)}{Ph\text{-}N(O^{\cdot})\text{-}N(COCH_3)\text{-}Ph} + Ph^{\cdot} + N_2 + HOCOCH_3 \qquad (ii)$$

$$Ph^{\cdot} + PhH \longrightarrow (II) \qquad (iii)$$

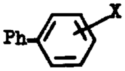
$$(I) + (II) \longrightarrow Ph\text{-}N(OH)\text{-}N(COCH_3)\text{-}Ph + Ph_2 \qquad (iv)$$

(Radical (I) is produced by addition of Ph· to the nitrosoamide).[1]

In an attempt to justify the molecule-induced decomposition (ii), we have now examined the reaction between benzenediazonium fluoroborate and diphenylhydroxylamine in aromatic solvents. The solvents selected were nitrobenzene and acetophenone, in which both reagents are soluble. In each case biaryls are produced by phenylation of solvent molecules, and the isomer distributions are characteristic of free radical substitution. The results, summarised in the table, are consistent with an initial reaction (v) analogous to (ii).

$$Ph_2NOH + PhN{:}NBF_4 \longrightarrow Ph_2NO\cdot + Ph\cdot + N_2 \quad HBF_4 \qquad (v)$$

Table



Solvent(PhX) (50ml)	g. Ph_2NOH	g. PhN_2BF_4	Total Yield (%)	Isomer Proportions %o	%m	%p
$PhNO_2$	0.72	0.5	42	64	9	28
"	"	"	35	58	10	32
"	1.2	"	26	60	10	30
"	0	"	6	21	58	21
PhCOMe	0.72	"	21.5	58.5	11.5	30
"	0	"	13	42	43	15

Typical isomer distribution for phenylation by Ph·:

Solvent (Temp.)	Reagent	Reference	%o	%m	%p
$PhNO_2$(20°)	nitrosoacetanilide	6	62.3	7.7	30
$PhNO_2$(80°)	benzoyl peroxide	7	61	10	29
$PhCO_2Me$* (80°)	benzoyl peroxide	7	58	17	25

Typical isomer distribution for phenylation by Ph^+:

Solvent (Temp.)	Reagent	Reference	%o	%m	%p
$PhNO_2$(60°)	$PhN_2^+BF_4^-$	5	20	81	0

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*Methyl benzoate appears to be the closest model for acetophenone for which literature figures exist concerning homolytic phenylation.

Reactions were carried out by adding, at room temperature, the solid diazonium salt to a freshly prepared and deoxygenated solution of diphenyl hydroxylamine which was vigorously stirred with calcium carbonate (to remove HBF_4) under nitrogen. The diazonium compound could not be detected in the reaction mixtures 2-3 minutes after addition was complete. During this time a high concentration of diphenyl nitroxide accumulated, as evidenced by electron spin resonance.

In the absence of the hydroxylamine, complete diazonium decomposition required hours or even days, after which time analysis showed very low yields of biaryl isomers in proportions suggestive of appreciable substitution by Ph^+.[5] In a further control reaction, m-chlorobenzenediazonium fluoroborate reacted with diphenylhydroxylamine in nitrobenzene to give 3-chloro-2'-, 3'-, and 4'-nitrobiphenyls, but no detectable 2-,3-, or 4-nitrobiphenyl.

These results provide a reasonable analogy for the key step in our suggested mechanism in the nitrosoamide reaction. We cannot discount an alternative scheme involving PhN=NO· and PhN=NOH.* However, oxidation of the arylcyclohexadienyl radical (II) either by PhN=NO· or by (I) might reasonably be expected to be very fast, possibly approaching diffusion control. Therefore the knowledge that (I) is present in the reactions at relatively high concentration, as monitored by E.S.R., makes (I) a likely candidate for the role of oxidant for (II). The molecule-induced homolysis (reaction v) is closely related to a reaction postulated by us[8] to occur between diphenylhydroxylamine and benzoyl peroxide:

$$Ph_2NOH + (PhCO_2)_2 \longrightarrow Ph_2NO\cdot + PhCO_2H + PhCO_2\cdot$$

This reaction has subsequently been studied by us in some detail[9] and has the characteristics of an electron-transfer process. Electron-transfer induced decomposition of diazonium salts is well-documented.[10]

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*Indeed Cadogan, Paton and Thomson have recently detected a weak esr signal due to a second radical in the reactions of nitrosoacetanilide with aromatic solvents, and have assigned the PhN:NO· structure to the radical responsible for this. We are grateful to Professor Cadogan for informing us of this result prior to publication.

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10. See for example J. F. Bunnett and H. Takayama, J. Org. Chem., 33, 1924 (1968); J. Am. Chem. Soc., 90, 5173 (1968).