Oxidation of Aromatic Amines with Hydrogen Peroxide Catalyzed by Cetylpyridinium Heteropolyoxometalates

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Received December 15, 1992

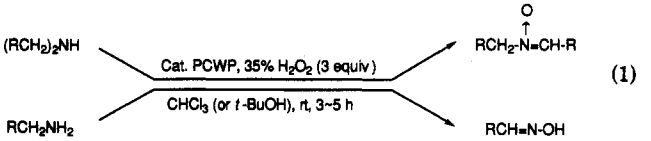
Various substituted anilines 1 were selectively converted into the corresponding nitrosobenzenes 2 or nitrobenzenes 3 by oxidation with aqueous hydrogen peroxide catalyzed by heteropolyoxometalates. The oxidations of anilines 1 with 35% H_2O_2 catalyzed by peroxotungstophosphate (PCWP) at room temperature in chloroform under two-phase conditions afforded nitrosobenzenes 2 with high selectivity. When the same reactions were carried out at higher temperature (e.g., refluxing chloroform), nitrobenzenes 3 were obtained in good yields. The oxidation of aniline (1a) with dilute H_2O_2 catalyzed by PCWP (2 wt %) in an aqueous medium produced azoxybenzene (4a) with high selectivity. Phenylazoxyalkanes 7 were prepared by the first direct cooxidation of 1a in the presence of primary aliphatic amines 6. For example, the oxidation of a 1:2 mixture of 1a and hexylamine (6b) with 35% H_2O_2 (6 equiv) in the presence of PCWP produced phenylazoxyhexane (7b) (51%) along with a small amount of 4a (8%). The reaction path for the conversion of anilines to azoxy-, nitroso-, and nitrobenzenes is described.

Both industry and academia have paid considerable attention to the heteropolyoxometalate-catalyzed oxidations of organic substrates with hydrogen peroxide.[1] Epoxidation of olefins,[2] oxidative cleavage of olefins and *vic*-diols,[2d,3] ketonization of alcohols and diols,[2d,4] conversion of alkynes into α,β-epoxy ketones,[5] etc. have been achieved by hydrogen peroxide oxidation with heteropolyoxometalate catalysts having a phase-transfer function.

The oxidation of amines is a fundamental reaction for the synthesis of O-containing amine derivatives. Therefore, a variety of oxidation methods have been explored. For example, aromatic amines can be oxidized not only with stoichiometric oxidants such as peracetic acid,[6] MnO_2,[7] $Pd(OAc)_4$,[8] and $Hg(OAc)_2$[9] but also with hydroperoxides by catalytic processes using B,[10] Ti,[11] Mo,[12] W,[13] Ru,[14] etc. In the oxidation of aniline, azobenzene,[7,10] azoxybenzene,[13,14] nitrobenzene,[6,15] and nitrosobenzene[8,13,16] have been formed; the product composition depends on the oxidants, catalysts, and reaction conditions employed. Although it is very difficult to control the selectivity in such reactions, it has been reported that quaternary ammonium salts influence the selectivity in the hydrogen peroxide oxidation of aniline to azoxybenzene and nitrobenzene.[14]

Azoxy compounds, especially mixed azoxy compounds with both aryl and alkyl groups, are of interest because of their physiological activity and their ubiquitous utilization in liquid crystals.[17] Only a limited number of methods have been reported for the preparation of mixed azoxy compounds.[18]

In a previous paper, we reported a preliminary study of the oxidation of amines with aqueous hydrogen peroxide under the influence of peroxotungstophosphate (PCWP, $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3\{PO_4[W(O)(O_2)_2]_4\}^{3-}$),[19] which can be easily prepared by treating 12-tungstophosphoric acid in 35% H_2O_2 with cetylpyridinium chloride in water (eq 1).[2d]



(1)

In this paper, we detail the results of the selective oxidation of a variety of aromatic amines to the corresponding nitroso or nitro compounds and the cooxidation of aromatic amines in the presence of aliphatic amines with aqueous hydrogen peroxide and heteropolyoxometalates as catalysts. The cooxidation provides a new direct route to aryl alkyl azoxy compounds.

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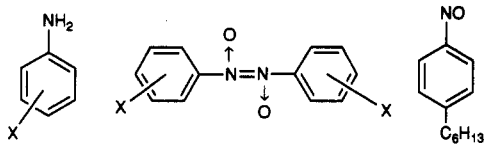
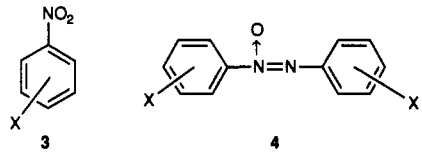
1. Oxidation of Aromatic Amines. Our primary interest was the selective oxidation of aromatic amines **1** to the corresponding nitrosobenzenes **2**, nitrobenzenes **3**, or azoxybenzenes **4**.



1 **2** **2c**



3 **4**

1, 2, 3, 4	X
a	H
b	4-CH_3
c	4-C_6H_{13}
d	4-Cl
e	4-NO_2
f	2-CO_2Me
g	3-CH_3, 5-CH_3
h	2-OH

Thus, we first examined the conversion of aniline (**1a**) into nitrosobenzene **2a**. The oxidations were carried out with 35% H_2O_2 as the oxidant and a heteropolyoxometalate as the catalyst under a varity of reaction conditions. The results of the aniline oxidations are summarized in Table I.

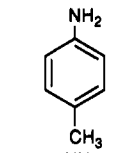
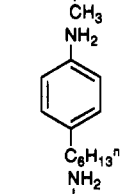
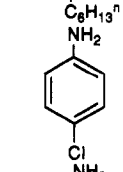
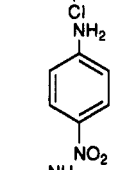
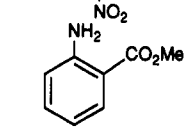
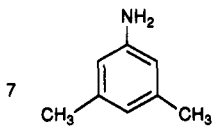
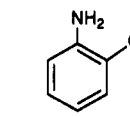
Table I. Oxidation of Aniline (1a) Catalyzed by Heteropolyoxometalates under Various Conditions[a]

			yield[b]/%	
run	catalyst	solvent	2a	3a
1	PCWP	$CHCl_3$	85	9
2	PCWP	*t*-BuOH	64	7
3	PCWP	MeOH	5	0
4[c]	PCWP	$CHCl_3$	33	6
5	PCMP	$CHCl_3$	75	0
6	PCMP	*t*-BuOH	13	0
7	PCMP	MeOH	3	0
8	CWP	$CHCl_3$	81	13
9	CWP	*t*-BuOH	67	5
10	CWP	MeOH	trace	0
11	WPA	$CHCl_3$	23	10
12	WPA	*t*-BuOH	75	10
13	WPA	MeOH	20	0

[a] **1a** (3 mmol) was allowed to react with 35% H_2O_2 (9 mmol) in the presence of catalyst (10 wt %) in solvent (7.5 mL) at rt for 2 h. [b] Determined by VPC. [c] PCWP (5 wt %).

Under two-phase conditions in chloroform, **1a** was oxidized with 3 equiv of 35% H_2O_2 in the presence of a catalytic amount of the heteropolyoxometalate (10 wt %) at room temperature for 2 h. After decomposition of unreacted hydrogen peroxide, the products were extracted with dichloromethane, isolated, and characterized; the yields were determined by GC using an internal standard technique.

Table II. Oxidation of Various Anilines to Nitrosobenzenes[a]

			yield[b]/%			
			nitrosobenzene		nitrobenzene	
run	substrate					
1	**1a**		**2a**	85	**3a**	9
2		**1b**	**2b**	80	**3b**	14
3[c]		**1c**	**2c**	71[d]	**3c**	13
4		**1d**	**2d**	47	**3d**	14
5		**1e**	**2e**	47[d]	**3e**	0
6[e]		**1f**	**2f**	64[d]	**3f**	19
7		**1g**	**2g**	57	**3g**	10
8		**1h**	complex mixture			

[a] Substrate (3 mmol) was allowed to react with 35% H_2O_2 (9 mmol) in the presence of PCWP (10 wt %) in $CHCl_3$ (7.5 mL) at rt for 2 h. [b] Determined by VPC. [c] 0 °C. [d] Isolated yield. [e] The reaction was carried out in refluxing $CHCl_3$ for 4 h.

A typical PCWP-catalyzed oxidation of **1a** gave **2a** in 85% yield along with a small amount of **3a**. Under homogeneous conditions with *tert*-butyl alcohol (*t*-BuOH) as the solvent, the yield of **2a** was slightly lower than that obtained from the two-phase chloroform system. The reaction was markedly retarded in methanol. The amount of PCWP also influenced the yields of **2a** and **3a** (run 4).

Although the catalytic activity of the corresponding molybdenum peroxo complex (PCMP) was lower than that of PCWP, **1a** was selectively oxidized in the presence of PCMP to give **2a** as the sole product without the formation of **3a**. Tris(cetylpyridinium) 12-tungstophosphate (CWP, $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3PW_{12}O_{40}^{3-}$) also efficiently catalyzed the oxidation. 12-Tungstophosphoric acid (WPA) was inadequate in the biphasic system but gave a considerable yield of **2a** in *t*-BuOH.

On the basis of these results, a wide variety of aromatic amines were oxidized with 35% H_2O_2 in the presence of PCWP at room temperature in the two-phase chloroform system. Representative results are summarized in Table II.

Table III. Oxidation of Various Anilines to Nitrobenzenes[a]

run	substrate		yield[b]/%
1	1a	3a	71
2	1b	3b	92
3	1c	3c	95[c]
4	1d	3d	87
5	1e	3e	78
6[d]	1f	3f	63
7[e]	1f	3f	81
8	1g	3g	78

[a] Substrate (3 mmol) was allowed to react with 35% H_2O_2 (9 mmol) in the presence of PCWP (10 wt %) in refluxing $CHCl_3$ (7.5 mL) for 4 h. [b] Determined by VPC. [c] Isolated yield. [d] After 24 h. [e] The reaction was carried out in refluxing *t*-BuOH for 24 h.

Like **1a**, *p*-toluidine (**1b**) was oxidized to the corresponding nitrosobenzene **2b** in satisfactory yield. The oxidation of 4-hexylaniline (**1c**) took place even at 0 °C to give 4-hexylnitrosobenzene (**2c**) in 71% isolated yield. However, 4-chloro- and 4-nitroanilines (**1d** and **1e**), bearing electron-withdrawing para substituents, were rather unreactive and formed the corresponding nitroso compounds **2d** and **2e**, in slightly lower yields. Methyl 2-aminobenzoate (**1f**) was difficult to oxidize under these conditions, but, in refluxing $CHCl_3$, **1f** was converted into methyl 2-nitrosobenzoate (**2f**) in 64% yield together with methyl 2-nitrobenzoate (**3f**) (19%). 3,5-Dimethylaniline (**1g**) gave nitroso derivative **2g** in 57% yield. However, a complex mixture was obtained from the oxidation of 2-aminophenol (**1h**).

Most of the nitrosobenzenes were isolated in dimeric form as yellowish solids, but **2c**, bearing a relatively long alkyl chain at the para position, was obtained in monomeric form and displayed the strong N→O stretching absorption at 1510 cm^{-1} characteristic of the monomer.[20] All of the nitrosobenzene dimers, except for **2a**, are believed to be trans because of the presence of N→O stretching absorption bands near 1250 cm^{-1}.[21] Nitrosobenzene dimers could easily be dissociated to monomers in chloroform to yield clean, green-colored solutions.

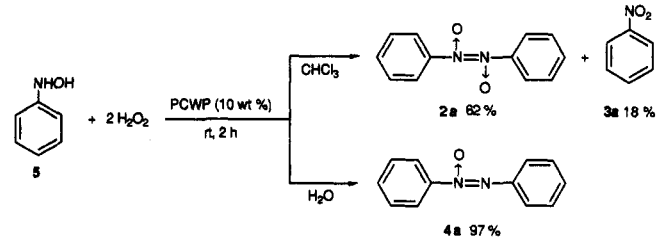
According to the literature, the oxidation of **1a** with either 30% H_2O_2 or a $RuCl_3$–H_2O_2 system in 1,2-dichloroethane[14] afforded azoxybenzene (**4a**) in 90% yield. Furthermore, it has been reported that the Na_2WO_4-catalyzed oxidation of **1a** with H_2O_2 (2 equiv) in water afforded a mixture of **2a** (16%) and **4a** (55%).[13] In contrast to these oxidations, the PCWP-catalyzed oxidation of **1a** under two-phase conditions gave **2a** rather than **4a**.

Although these heteropolyoxometalate-catalyzed oxidations of aromatic amines (except for **1f**) gave nitrosobenzenes in good yields at room temperature, the same oxidations at higher temperature (e.g., refluxing chloroform) gave nitro compounds **3** with high selectivities (Table III).

For instance, **1a** was oxidized by the PCWP–H_2O_2 system in refluxing chloroform to give nitrobenzene (**3a**) in 71% yield. Similar results were obtained in the oxidations of various anilines with electron-donating or electron-withdrawing substituents. Anilines **1c** and **1d** were oxidized to the corresponding nitro compounds, **3c** and **3d**, respectively, in good yields. Methyl 2-aminobenzoate (**1f**) was oxidized to methyl 2-nitrobenzoate (**3f**) at 65 °C (refluxing chloroform) for 24 h in moderate yield (63%). To obtain **3f** in satisfactory yield, a higher temperature was necessary. Nitrobenzene **3f** was obtained in 81% yield when the oxidation was carried out at 85 °C (refluxing *t*-BuOH) for 24 h. In the case of **1g**, 3,5-dimethylnitrobenzene (**3g**) was formed in 78% yield.

In order to clarify the reaction path of the present oxidation, we examined the oxidations of **2a** and **4a** with 35% H_2O_2 (2 equiv) in the presence of PCWP (10 wt %) in chloroform at room temperature. Under these conditions the oxidation of **2a** produced exclusively nitrobenzene (**3a**) in 80% yield. However, **4a**, which was expected to be easily oxidized to nitrosobenzene (**2a**), was resistant to the oxidation and was recovered unchanged. This fact suggested that **3a** was the product of further oxidation of **2a** not **4a**.

To obtain more information about the way in which **2a** was formed, we subjected a possible reaction intermediate, *N*-phenylhydroxylamine (**5**), which was not detected during the oxidation of **1**,[22] to oxidation by the PCWP–H_2O_2 system. The products of the oxidation of **5** depended markedly on the reaction medium employed (eq 2). The



(2)

oxidation of **5** in chloroform afforded **2a** and **3a** in 62% and 18% yields, respectively, but only a trace amount of **4a** was formed. A rather surprising finding was that, in an aqueous medium with dilute hydrogen peroxide (5% H_2O_2), **5** produced exclusively **4a** in quantitative yield (97%). Thus, we expected that the oxidation of **1a** in an aqueous medium would give a result similar to that observed in the oxidation of **5**. In fact, the oxidation of **1a** with 10% H_2O_2 under the influence of PCWP (10 wt %) produced azoxybenzene (**4a**) (42%) in preference to nitrosobenzene **2a** (35%) and nitrobenzene (**3a**) (11%). When the amount of the PCWP used was reduced to 2 wt %, **4a** was obtained in 71% yield along with a small quantity of **2a** (7%).

It is particularly important that **4a** was formed in almost quantitative yields (95%) from the condensation of **2a** with **5** in both water and chloroform at room temperature. The fact that the condensation of **2a** with **5** proceeded readily even in chloroform showed that the aqueous medium was required for the generation of *N*-phenylhydroxylamine (**5**), a key intermediate for the specific transformation of **1a** to **4a**. In addition, it was found that the reaction of **2a** with **1a** in water at room temperature gave **4a** as expected, though the yield was low (20%). However, when the same reaction was carried out in chloroform, starting materials **1a** and **2a** were recovered.

Because of the complexity of the reaction, the variety of products, and two-phase conditions used for the reaction, it seemed rather hazardous to make an exact assessment

(20) Pouchert, C. J. In *The Aldrich Librang of Infrared Spectra*; Aldrich Chemical Co. Inc.: Milwaukee, 1975; p 591.

(21) It has been reported that *cis*-nitrosobenzene dimers have a strong N→O stretching absorption near 1400 cm^{-1}.[20] The IR spectrum of **2a** was in fair agreement with that expected for the *cis*-form.[20]

(22) We believe that **5** is difficult to detect in the course of the reaction owing to its rapid oxidation to **2a**.

of the reaction path. However, we may make some assumptions that agree with the experimental results.

In the oxidations of **1a** and **5** by the two-phase PCWP-H_2O_2 system with chloroform, **2a** was produced along with **3a**, the product of further oxidation of **2a**. In contrast, the oxidations of **1a** and **5** in the aqueous medium led to the highly selective formation of **4a** rather than **2a**. The results obtained for the oxidations of **1a** were very similar to those for **5**. On the basis of these results, we believe that the majority of **4a** was indeed formed through the condensation between **5** and **2a**.

However, it cannot be decided at the present time whether or not the oxidation of **1a** to **2a** proceeds via the formation of **5** as an intermediate. Because of the preferential formation of **2a** in chloroform, it seems likely that the oxidation of **5** to **2a** occurs more easily than the condensation of **5** with **2a** to give **4a**.

For the formation of **2a** from **1a**, a direct path that does not involve **5** as an intermediate may be possible because **1a** is smoothly oxidized by the peroxo oxygen of PCWP in a nonaqueous medium with chloroform as the solvent at room temperature to give **2a** (58%) and **3a** (6%) as well as a trace amount of **4a**. Under such nonaqueous conditions, it is difficult for **5** to be formed from **1a**.

2. Cooxidation of Aromatic Amines and Alkylamines. Unsymmetrical azoxy compounds are usually synthesized by the oxidation of the corresponding azo compounds or by condensation between nitroso compounds and hydroxylamines.[18] For the preparation of aromatic azoxyalkanes, substitution of nitrosohydroxylamine tosylates (ArN(O)=NOTs) with alkyl Grignard reagents has been employed.[23]

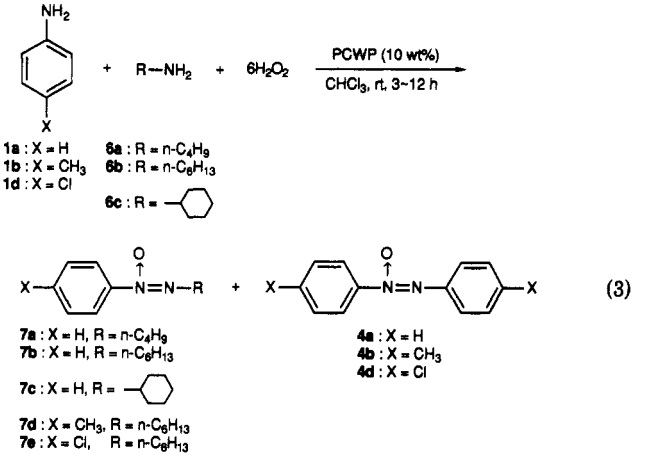
Although the separate oxidation of aromatic amines and alkylamines by the PCWP–H_2O_2 system produced nitroso compounds and oximes, respectively,[19] we found that the cooxidation of aromatic amines and alkylamines by this system gave arylazoxyalkanes in fair yields (eq 3) (Table IV). This is the first direct route to arylazoxyalkanes from aromatic amines and alkylamines.

Table IV. Co-oxidation of Aromatic Amines and Alkylamines to Arylazoxyalkanes[a]

run	aromatic amine	alkylamine (equiv)	PCWP (wt %)	time (h)	yield[b]/%	
1	**1a**	**6a** (1)	10	3	**7a** (43)	**4a** (9)
2	**1a**	**6b** (2)	20	3	**7b** (51)	**4a** (8)
3	**1a**	**6c** (3)	20	3	**7c** (50)	**4a** (9)
4[c]	**1b**	**6b** (2)	10	15	**7d** (27)	**4b** (18)
5[c]	**1d**	**6b** (2)	10	15	**7e** (21)	**4d** (trace)

[a] A mixture of 1 (3 mmol) and 6 (3–9 mmol) was oxidized with 35% H_2O_2 (18 mmol) in the presence of PCWP (10 wt % to 1) in $CHCl_3$ (7.5 mL) at rt. [b] GC yields based on the amount of aromatic amines used. [c] 10% H_2O_2 and $CHCl_3$ (15 mL) were used.

In a typical cooxidation of aniline (**1a**) and butylamine (**6a**) with 35% H_2O_2 (6 equiv) in the presence of PCWP (10 wt % to **1a**) in chloroform, *N*-phenyl-*N'*-1-butyldiimide *N*-oxide (phenylazoxybutane) (**7a**) was formed in 43% yield along with a small amount (9%) of azoxybenzene (**4a**). The structure of **7a** was determined by comparison of its NMR spectrum with that reported in the literature.[23,24] The reaction of **1a** with hexylamine (**6b**) or cyclohexylamine (**6c**) gave *N*-phenyl-*N'*-1-hexyldiimide *N*-oxide (**7b**) and *N*-phenyl-*N'*-1-cyclohexyldiimide *N*-oxide (**7c**) in 51% and 50% yields, respectively. In contrast, *p*-toluidine and 4-chloroaniline (**1b** and **1d**) in the presence of **6b** were converted into the corresponding azoxy compounds (**7d** and **7e**) in slightly lower yields.



In these reactions, an alternative azoxy compound, in which the oxygen atom is attached to the nitrogen atom bearing the alkyl group, was not obtained.

Table V shows representative results for the cooxidation of **1a** and **6b** under several reaction conditions.

Table V. Cooxidation of Aniline (1a) and Hexylamine (6b) with H_2O_2 by PCWP under Several Conditions[a]

run	ratio of **1a**/**6b**	PCWP (wt %)	H_2O_2 (equiv)	yield[b]/% **7b**	**4a**
1	1/1	10	6	23	18
2	1/1	20	6	36	19
3	1/2	20	6	51	8
4[c]	1/3	20	6	trace	trace
5[d]	1/1	10	6	32	20

[a] A mixture of **1a** (3 mmol) and **6b** (3~9 mmol) was oxidized with 35% H_2O_2 (6 equiv) in the presence of PCWP (10–20 wt % to **1a**) in $CHCl_3$ at rt. [b] GC yields based on **1a** used. [c] A complex mixture was formed. [d] *t*-BuOH was used as solvent.

The oxidation of a 1:1 mixture of **1a** and **6b** produced nearly equal amounts of **7b** (23%) and **4a** (18%). Phenylazoxyhexane (**7b**) was selectively formed in preference to **4a** when 2 equiv of aliphatic amine **6b** were allowed to react with **1a** (run 3). However, when the reaction was carried out with a 2-fold excess of **6b**, a complex mixture was obtained, and a considerable amount of heat evolved during the reaction. When the reaction was carried out in *t*-BuOH, **7b** was obtained in fair yield. It is interesting to note that azoxybenzene (**4a**), which was not formed by the oxidation of **1a** alone under these conditions, was obtained in the cooxidation of aniline (**1a**) and aliphatic amines **6a** and **6b**.

Several reactions were carried out to clarify the reaction path for the formation of azoxy compounds from **2a** and **6b** (Table VI).

First, a 1:1 mixture of **2a** and **6b** was allowed to react both in the absence and in the presence of PCWP in chloroform at room temperature for 12 h. With PCWP, **4a** was obtained in 26% yield and, without PCWP, in 30% yield; but in both cases only small quantities of phenylazoxyhexane (**7b**) were formed. When the mixture was treated with 35% H_2O_2 (1 equiv), a large amount of nitrobenzene (**3a**) (44%) was formed instead of **7b** (3%). However, when the reaction was performed in the presence

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(24) Freeman, J. P. *J. Org. Chem.* **1963**, *28*, 2508.

Table VI. Reactions of Nitrosobenzene (2a) with Hexylamine (6b) under Several Reaction Conditions[a]

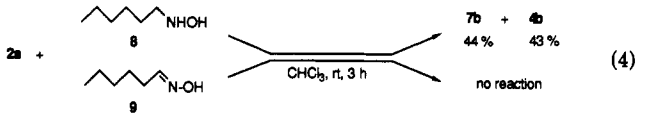
run	catalyst	H_2O_2 (equiv)	time (h)	yield/% 7b	yield/% 4a
1			12	trace	30
2	PCWP		12	5	26
3[b]		1	12	3	1
4	PCWP	1	3	43	20
5		1	3	2	6

[a] **2a** (1 mmol) as a monomer was allowed to react with **6b** (1 mmol) in the presence or absence of PCWP (10 wt ‰ wit respect to **2a**) in $CHCl_3$ (7.5 mL) at rt. [b] Nitrobenzene **3a** (44%) was formed.

of both PCWP and 35% H_2O_2 (1 equiv), **7b** (43%) was formed in preference to **4a** (20%).

Freeman[24] and Taylor et al.[18b] have reported the formation of phenylazoxymethane from the reaction of nitrosobenzene with N-methylhydroxylamine. Hydroxylamines are considered to be precursors of oximes in the oxidation of primary amines.[13] Hence, we suggest that alkylhydroxylamines, formed in the course of the cooxidation of **1a** and **6**, react with **2a** to give phenylazoxyalkanes **7a** and **7b**. In fact, the reaction of **2a** with *N*-hexylhydroxylamine (**8**), prepared independently from the reduction of *N*-hexylaldoxime (**9**) with $NaBH_4$,[25] in chloroform at room temperature gave mixed azoxyalkane **7b** in 44% yield together with azoxybenzene (**4a**) (43%) (eq 4). The reaction in the presence of PCWP (10 wt % to **2a**) gave almost the same results; **7b** (50%) and **4a** (41%) were formed.

We also examined the reaction of **2a** with hexylaldoxime **9**, but no reaction took place.



(4)

In summary, we have shown that the oxidation of anilines with 35% H_2O_2 catalyzed by PCWP under two-phase conditions with chloroform as the solvent at room temperature provides a simple, general procedure for the preparation of various substituted nitroso compounds that are difficult to prepare selectively by the conventional method. The same oxidation carried out at reflux temperature offers the highly selective conversion of anilines into nitro compounds. The cooxidation of aniline and aliphatic primary amines provides a direct route to phenylazoxyalkanes. The reaction path for the conversion of aniline (**1a**) to azoxybenzene (**4a**), nitrosobenzene **2a**, and nitrobenzene (**3a**) by H_2O_2 in the presence of PCWP is discussed.

Experimental Section

General Procedures. Unless otherwise noted, all starting materials were commercially available and were used without further purification. GLC analyses were performed with a flame ionization detector using a 2-m × 3-mm column packed with silicone OV-17 or SE-30. ^1H and ^{13}C NMR were measured at 400 and 100 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. The yields of products estimated from the peak areas depended on the internal standard technique used.

Preparation of Peroxo Complex PCWP and PCMP. To a solution of WPA (11.5 g, ca. 4 mmol) of 35% H_2O_2 (200 mL) was added dropwise CPC (4.3 g, 12 mmol) in H_2O (40 mL), and the mixture was stirred at 40 °C for 24 h. After the suspended mixture was cooled to room temperature, the resulting white precipitate was filtered and then washed several times with distilled water and dried in vacuo to give PCWP (ca. 5 g, 60%): IR (nujol) 2900, 2850, 1633, 1486, 1466, 1090, 1055, 957, 842, 774, 722, 684, 648, 625, 571, 552, 524 cm^{-1}. Anal. Calcd for $C_{63}H_{114}N_3O_{24}PW_4$ (PCWP): C, 36.66; H, 5.57; N, 2.04. Found: C, 36.41; H, 5.47; N, 2.01.

PCMP was prepared by the method reported previously:[26] IR (KBr) 3400, 2900, 2850, 1630, 1480, 1460, 1165, 1070, 990, 865, 590, 540 cm^{-1}. Anal. Calcd for $C_{63}H_{114}N_3O_{24}PMo_4$ (PCMP): C, 44.19; H, 6.71; N, 2.45. Found: C, 43.66; H, 6.87; N, 2.42.

Preparation of Tris(cetylpyridinium) 12-Tungstophosphate $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3(PW_{12}O_{40})^{3-}$ (CWP). To a solution of CPC (1.87 g, 5.22 mmol) in 70 mL of water was added dropwise WPA (5.01 g, 1.74 mmol) in 10 mL in water with stirring at ambient temperature. A white precipitate formed immediately. After being stirred continuously for 3–4 h, the resulting mixture was filtered, washed several times with distilled water, and dried in vacuo to give CWP in 80–90% yield: IR (KBr) 3350, 2900, 2850, 1630, 1480, 1455, 1160, 1070, 970, 885, 820–750, 670, 500 cm^{-1}. Anal. Calcd for $C_{63}H_{114}N_3PW_{12}O_{40}$: C, 19.96; H, 3.03; N, 1.11. Found: C, 20.27; H, 3.08; N, 1.08.

General Procedure for Oxidation of Aromatic Amines 1 to Nitrosobenzenes 2. To a stirred solution of PCWP (10 wt %) and 35% H_2O_2 (9 mmol) in $CHCl_3$ (7.5 mL) was added the appropriate aromatic amine (3 mmol), and the mixture was stirred at room temperature for 2 h. The product was extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The product was purified by column chromatography on silica gel (1/5–10 ethyl acetate/hexane). The melting point and spectral data of each product were compared with those of authentic samples and the literature values.[8]

General Procedure for Oxidation of Aromatic Amines 1 to Nitrobenzenes 3. To a stirred solution of PCWP (10 wt %) and 35% H_2O_2 (9 mmol) in $CHCl_3$ (7.5 mL) was added the appropriate aromatic amine (3 mmol), and the mixture was allowed to react at the reflux temperature for 4 h. The product was extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The product was purified by column chromatography on silica gel (1/5–10 ethyl acetate/hexane).

Nitrosobenzene as a dimer (2a): mp 65–67 °C (lit.[8] mp 68 °C); IR (KBr) 3060, 1482, 1396, 1189, 1071, 948, 763, 688 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.90–7.88 (d, J = 8.4 Hz, 4H), 7.72–7.68 (m, 2H), 7.63–7.59 (t, J = 8.1 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.8, 135.6, 129.3, 120.9.

4-Methylnitrosobenzene as a dimer (2b): mp 47–49 °C (lit.[8] mp 47.5–48 °C); IR (KBr) 3048, 1655, 1602, 1508, 1452, 1409, 1230, 1254, 1185, 1119, 846, 821, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.81–7.79 (d, J = 8.1 Hz, 4H), 7.40–7.37 (d, J = 8.1 Hz, 4H), 2.44 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.6, 147.2, 121.2, 21.9.

4-Hexylnitrosobenzene as a monomer (2c): green oil: IR (neat) 2929, 2857, 1601, 1510, 1457, 1142, 1345, 1184, 1118, 834 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.15–8.13 (d, J = 8.6 Hz, 2H), 7.84–7.82 (d, J = 8.6 Hz, 2H), 2.71–2.67 (t, J = 8.0 Hz, 2H), 1.68–1.62 (m, 2H), 1.32–1.30 (m, 6H), 0.90–0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.7, 152.1, 123.6, 121.3, 36.3, 31.6, 30.8, 28.9, 22.5, 14.1.

4-Chloronitrosobenzene as a dimer (2d): mp 85–87 °C (lit.[8] mp 85–87 °C); IR (KBr) 3098, 1582, 1482, 1403, 1259, 1090, 1014, 856, 817, 546, 506, 449 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.87–7.85 (d, J = 8.6 Hz, 4H), 7.40–7.37 (d, J = 8.6 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.7, 142.4, 129.7, 122.2.

4-Nitronitrosobenzene as a dimer (2e): mp 110–112 °C; IR (KBr) 3111, 1528, 1349, 1263, 1109, 857, 839, 749, 710, 689 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.54–8.52 (d, J = 8.8 Hz, 4H), 8.08–8.06 (d, J = 8.8 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.5, 125.5, 124.9, 121.4.

Methyl 2-Nitrosobenzoate as a Dimer (2f). To a stirred solution of PCWP (10 wt %) and 35% H_2O_2 (9 mmol) in $CHCl_3$

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(26) Ishii, Y.; Yamawaki, K.; Yoshida, T.; Ura, T.; Ogawa, M. *J. Org. Chem.* **1987**, *52*, 1868.

(7.5 mL) was added methyl 2-aminobenzoate (**1f**) (3 mmol), and the mixture was allowed to react at the reflux temperature for 4 h. The product was extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. Recrystallization ($CHCl_3$) gave **2f** in 64% yield: mp 105–106 °C; IR (KBr) 2958, 1719, 1602, 1489, 1466, 1434, 1267, 1194, 1166, 1132, 1086, 963, 818, 800, 751, 697, 669, 620, 448 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.15–8.13 (d, J = 7.7 Hz, 1H), 7.91–7.89 (d, J = 7.7 Hz, 1H), 7.82–7.78 (t, J = 7.7 Hz, 1H), 7.65–7.61 (t, J = 7.7 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.7, 141.9, 134.1, 131.5, 130.7, 125.3, 124.6, 52.7. Anal. Calcd for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.57; H, 4.28; N, 8.53.

3,5-Dimethylnitrosobenzene as a dimer (2g): mp 56–57 °C; IR (KBr) 3089, 2918, 1612, 1473, 1372, 1227, 1154, 1049, 861, 782, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.82 (s, 4H), 7.50 (s, 2H), 2.61 (s, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.6, 139.2, 137.0, 119.3, 21.2. Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.08; H, 6.71; N, 10.36. Found: C, 71.39; H, 6.85; N, 10.53.

Methyl 2-Nitrobenzoate (3f). To a stirred solution of PCWP (10 wt %) and 35% H_2O_2 (9 mmol) in t-BuOH (7.5 mL) was added methyl 2-aminobenzoate (**1f**) (3 mmol), and the mixture was allowed to react at the reflux temperature for 24 h. The product was extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. Column chromatography (SiO_2, ethyl acetate) gave **3f** in 81% yield.

Oxidation of *N*-Phenylhydroxylamine (5) to Nitrosobenzene 2a or Azoxybenzene (4a). Compounds **5** (3 mmol) was added to a stirred solution of PCWP (10 wt %) and either 35% H_2O_2 (6 mmol) in $CHCl_3$ (7.5 mL) or 5% H_2O_2 (6 mmol) in the absence of $CHCl_3$, and the mixture was allowed to react at room temperature for 2 h. The product was extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure to give **2a** or **4a**, respectively, as principal product.

Oxidation of Aniline (1a) to Azoxybenzene (4a). To a stirred solution of PCWP (2 wt %) and 10% H_2O_2 (2 mmol) was added **1a** (1 mmol), and the mixture was allowed to react at room temperature for 8 h. The product was extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under the reduced pressure. Product **4a** was purified by column chromatography on silica gel (1/5 ethyl acetate/hexane): mp 35–36 °C (lit.[18a] mp 34.5–35.5 °C); IR (KBr) 1479, 1438, 762, 684 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.32–8.30 (d, J = 8.4 Hz, 2H), 8.17–8.16 (d, J = 8.4 Hz, 2H), 7.58–7.25 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.3, 144.0, 131.6, 129.6, 128.8, 128.7, 125.5, 122.3. Anal. Calcd for $C_{12}H_{10}N_2O$: C, 72.53; H, 5.03; N, 14.09. Found: C, 72.78; H, 5.09; N, 14.14.

Condensation of Nitrosobenzene 2a with *N*-Phenylhydroxylamine (5) to Azoxybenzene (4a). To a stirred solution of **5** (3 mmol) in H_2O (7.5 mL) or $CHCl_3$ (7.5 mL) was added **2a** (3 mmol), and the mixture was stirred at room temperature for 3 h. The product was extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure to give almost pure **4a**.

Reaction of Aniline (1a) with Nitrosobenzene 2a in Water. To a stirred solution of **2a** (1 mmol) in H_2O (1.8 mL) was added **1a** (1 mmol), and the mixture was stirred at room temperature for 16 h. The product was extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. Product **4a** was purified by column chromatography on silica gel (hexane, eluent).

Oxidation of *N*-Phenylhydroxylamine (5) with PCWP. A mixture of **5** (1 mmol) and PCWP (1.29 g) was stirred in $CHCl_3$ (10 mL) at room temperature of 3 h. After the solution was added to ethyl acetate (10 mL), the resulting precipitate was filtered and the product was extracted with dichloromethane. The products, **2a** and **3a**, were purified by column chromatography on silica gel (1/5 ethyl acetate/hexane).

General Procedure for Oxidation of a Mixture of Aromatic Amines 1 and Alkylamines 6 to Azoxybenzenes 7. To a stirred solution of PCWP (10 wt %) and 35% H_2O_2 (18 mmol) in $CHCl_3$ (7.5 mL) was added an aromatic amine **1** (3 mmol) and alkylamine **6** (3–9 mmol), and the mixture was stirred at room temperature for 3 h. The product was extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The product was purified by HPLC.

***N*-Phenyl-*N'*-butyldiimide *N*-oxide (7a)**: IR (neat) 2959, 2932, 2873, 1484, 1444, 1420, 1342, 1306, 1217, 1172, 1118, 1069, 1025, 825, 775, 751, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.16–8.14 (d, J = 8.4 Hz, 2H), 7.54–7.26 (m, 3H), 3.70–3.67 (t, J = 7.0 Hz, 2H), 1.88–1.81 (hept, J = 7.3 Hz, 2H), 1.55–1.48 (sextet, J = 7.3 Hz, 2H), 1.01–0.98 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.2, 131.4, 128.7, 128.6, 124.2, 122.0, 52.57, 29.4, 21.1, 13.9.

***N*-Phenyl-*N'*-hexyldiimide *N*-oxide (7b)**: IR (neat) 2930, 2858, 1483, 1420, 1344, 1306, 1172, 1068, 776, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.16–8.14 (d, J = 8.4 Hz, 2H), 7.54–7.44 (m, 3H), 3.69–3.66 (t, J = 7.1 Hz, 2H), 1.89–1.82 (hept, J = 7.1 Hz, 2H), 1.52–1.47 (m, 2H), 1.38–1.34 (m, 4H), 0.93–0.90 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.3, 131.4, 128.7, 122.0, 52.9, 31.4, 27.6, 27.3, 22.6, 14.1. Anal. Calcd for $C_{12}H_{18}N_2O$: C, 69.86; H, 8.80; N, 13.58. Found: C, 69.76; H, 8.76; N, 13.54.

***N*-Phenyl-*N'*-cyclohexyldiimide *N*-oxide (7c)**: IR (neat) 2931, 2856, 1478, 1440, 1344, 1348, 1318, 1301, 1258, 1172, 1069, 1022, 961, 928, 890, 860, 776, 695 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.15–8.13 (d, J = 7.7 Hz, 2H), 7.53–7.43 (m, 3H), 4.29–4.21 (m, 1H), 1.98–1.92 (m, 2H), 1.86–1.79 (m, 2H), 1.71–1.66 (m, 2H), 1.55–1.37 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.7, 131.3, 128.6, 122.1, 59.0, 29.4, 25.9, 24.4. Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.89; N, 13.71. Found: C, 70.49; H, 7.97; N, 13.82.

***N*-(4-Methylphenyl)-*N'*-hexyldiimide *N*-oxide (7d)**: IR (neat) 2956, 2930, 2858, 1499, 1475, 1420, 1343, 1306, 1177, 1108, 1019, 828, 757, 717, 677 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.04–8.02 (d, J = 8.4 Hz, 2H), 7.24–7.22 (d, J = 8.4 Hz, 2H), 3.67–3.64 (t, J = 7.1 Hz, 2H), 2.41 (s, 3H), 1.88–1.80 (hept, J = 7.3 Hz, 2H), 1.49–1.34 (m, 6H), 0.93–0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.2, 141.9, 129.2, 121.9, 52.8, 31.6, 27.6, 27.3, 22.6, 21.3, 14.1.

4-Methylazoxybenzene (4b): mp 69–70 °C (lit.[18a] 66–68 °C); IR (neat) 2959, 2932, 2872, 1483, 1420, 1306, 1166, 1069, 1024, 842, 756, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.18–8.16 (d, J = 8.4 Hz, 2H), 8.12–8.10 (d, J = 8.4 Hz, 2H), 7.27–7.2 (m, 4H), 2.42 (s, 3H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.2, 141.9, 140.0, 129.3, 125.7, 121.1, 21.5, 21.3.

***N*-(4-Chlorophenyl)-*N'*-hexyldiimide *N*-oxide (7e)**: IR (neat) 2931, 2858, 1586, 1479, 1420, 1345, 1308, 1170, 1093, 1014, 828, 841, 758, 720, 671 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.13–8.11 (d, J = 9.0 Hz, 2H), 7.44–7.42 (d, J = 9.0 Hz, 2H), 3.67–3.64 (t, J = 7.0 Hz, 2H), 1.88–1.80 (hept, J = 7.1 Hz, 2H), 1.50–1.46 (m, 2H), 1.38–1.34 (m, 4H), 0.93–0.90 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.5, 137.7, 128.8, 123.4, 52.9, 31.6, 27.6, 27.2, 22.6, 14.0.

Condensation of Nitrosobenzene (2a) with *N*-Hexylhydroxylamine (8) to Phenylazoxyhexane (7b). To a stirred solution of **8** (1 mmol) in $CHCl_3$ (2.5 mL) was added **2a** (1 mmol), and the mixture was stirred at room temperature for 3 h. The product was extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The products, **7b** and **4a**, were obtained by the workup described above.

Supplementary Material Available: ^1H and ^{13}C NMR spectra (19 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.