Summary

Acylarylamino compounds having chloro or methoxyl group at *meta-* or *para-*position of benzene ring were oxidized with hydrogen peroxide in varied conditions. In the case of introduction of electron-attracting group, yields of nitro compounds were fairly good and at the same time, considerable amounts of the starting materials were recovered, while, in the case of electron-releasing group, yields of nitro compounds were poor and almost none of the starting materials was recovered. Reasonable explanations of these phenomena were discussed.

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49. **Haruyuki Ito** : Synthesis of Nitro Compounds by Means of Oxidation of Acylamino Compounds. XI.[*1] Oxidation of Alkylamino Compounds with Hydrogen Peroxide.

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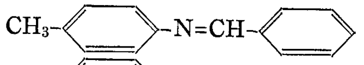
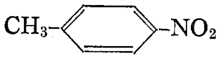
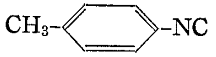
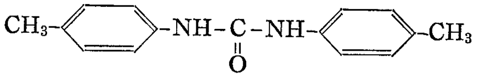
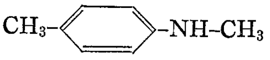
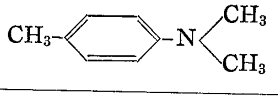
In the previous paper of this series,[1] it has been reported that the oxidation of various aromatic acylamino compounds with hydrogen peroxide proceeded to form aromatic nitro compounds. In order to extend the scope of this reaction, various nitrogen compounds were oxidized with hydrogen peroxide, and the result of the reactions which afforded nitro compounds in considerable yields was shown in Table I.

Table I. Result of Oxidation of Various Aromatic Nitrogen Compounds with Hydrogen Peroxide

No.	Starting materials	Products	Yields (%)
1			5.0
2		〃	22.5
3		〃	26.3
4		〃	35.4
5		〃	5.0

N-Benzylidene-*p*-toluidine (No.1) may be oxidized through the similar route to quinoline,[2] since both have partially the azomethine structure. *p*-Isocyanotoluene (No.2) was readily converted into 1,3-ditolylurea by way of isocyanate during the hydrogen

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[*1] Part X : This Bulletin, 12, 329 (1964).

[*2] Oshika, Shizuoka (伊藤晴之).

1) T. Kosuge, *et al.* : Kenkyu Nenpo (Faculty of Pharm. Univ. of Kanazawa) 2, 10 (1952).

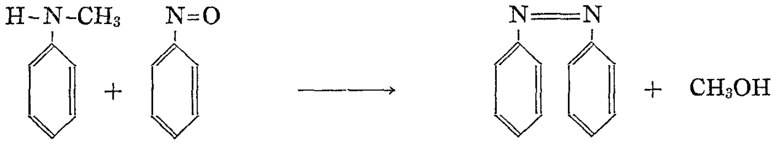
2) T. Kosuge : This Bulletin, 2, 397 (1954).

peroxide treatment (46% yield), suggesting that the oxidation is analogous to that of No. 3. The oxidation of 1,3-ditolylurea (No. 3) may occur by the mechanism discussed in the Part Ⅸ[3] of this series, since the derivative of urea is included in the acylamino compounds. The oxidations Nos. 4 and 5 provide the interesting reaction to be examined precisely, and it is the main purpose of this paper to report details about the oxidation of aromatic alkylamino compounds with hydrogen peroxide.

The Reaction Mechanism

N-Methyl-*p*-toluidine was warmed with eight moles of hydrogen peroxide for a few minutes. Violent reaction took place and 4,4′-dimethylazobenzene came out as orange precipitate in 12.1% yield. The yield increased in much milder condition; *viz.*, the yield of 4,4′-dimethylazobenzene was raised to 22.5%, when oxidized with one mole of hydrogen peroxide at room temperature for twenty hours.

Nitrosotoluene was found to be an intermediate of this reaction. At the first period of the reaction, oily green distillate was observed in the reflux condenser, and therefore, the green oil was isolated by steam distillation after decomposition of the excess of hydrogen peroxide with formic acid. This oil was identified as *p*-nitrosotoluene by converting into 4-methyl-4′-carboxylazobenzene. These results suggested that the azo compound was produced by the reaction between the starting material and the intermediate. In fact, the nitroso compound was reacted with alkylamino compound to produce azobenzene and 4,4′-dimethylazobenzene, was obtained in almost theoretical yield by condensing N-methyl-*p*-toluidine with *p*-nitrosotoluene in petroleum ether at room temperature.



In ordinary or more violent condition of the oxidation, both nitro compounds and azoxy compounds were obtained. The former was produced from nitroso compounds by further oxidation with hydrogen peroxide.

From the fact that the nitroso compound plays the part of an intermediate, it was assumed that the oxidation reaction of aromatic alkylamino derivatives proceed under the mechanism analogous to the oxidation of acyl amino compounds.

In papers of oxidations of alkylarylamines or dialkylamines with potassium permanganate[4] or manganese dioxide,[5] it was reported that alkyl groups attached to nitrogen atoms of arylamines were oxidized to acyl groups in fairly good yields. If, in this hydrogen peroxide oxidation of the alkylarylamine, the oxidation of alkyl group at nitrogen would take place to afford the N-acyl compound, this oxidation reaction is included in the oxidation of the acylamino compounds, whose mechanism was discussed in Part Ⅸ.[3] However, the following facts were inconsistent with the experimental data of the oxidation of the acylamino compounds. (i) A considerable amount of azo or azoxy compound was obtained in this case (Table Ⅲ, *vide infra*). (ii) The yields of nitro compounds from dialkylarylamines were too small (Table Ⅴ), if the oxidation were assumed to pass through acylamines, which afforded nitro compounds in good yields at the subsequent experiments (Table Ⅳ).

Therefore, a mechanism as shown in Chart 1 is considerable for the hydrogen peroxide oxidation of the alkylamino compound.

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[3] H. Ito : This Bulletin, **12**, 326 (1964).
[4] R. Willstätter : Ber., **33**, 1169 (1900).
[5] H.B. Henbest, A. Thomas : J. Chem. Soc., **1957**, 3032; E. Wenkert : Experientia, **10**, 346 (1954).

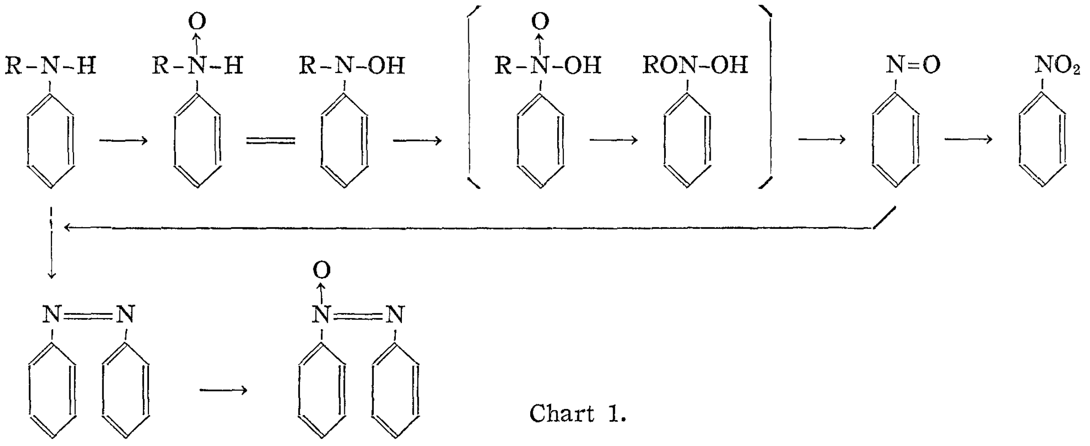
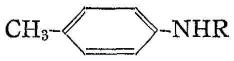


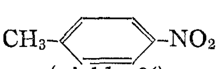
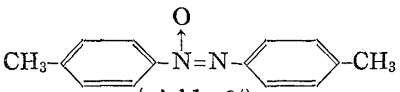
Chart 1.

Effect of Alkyl Functions Substituted on Nitrogen Atoms

The effect of alkyl functions substituted on nitrogen atom of *p*-toluidine was investigated, and for that purpose, the starting materials were obtained by hydrolysis of pure N-alkyl-N-tosyl-*p*-toluidines. The amount of acetic acid used as solvent was 1.2 times of 30% hydrogen peroxide in volume, and the oxidation was carried out at 100° for seven hours. The yields of *p*-nitrotoluene and 4,4′-dimethylazoxybenzene were listed in Table II.

TABLE II. Result of Oxidation of N-Alkyl-*p*-toluidine



No.	R	H_2O_2 (mole ratio)	 (yield, %)	 (yield, %)
1	CH_3	8	22.0	13.4
2	〃	12	29.0	6.4
3	〃	18	35.4	4.9
4	C_2H_5	12	21.1	4.8
5	〃	18	26.6	3.1
6	C_3H_7	12	18.4	6.5
7	〃	18	24.8	4.2

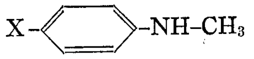
The yield of *p*-nitrotoluene decreased in accordance with increase of the number of carbon atoms of alkyl functions, suggesting the sterical effect of alkyl groups on N-oxidation. The increase of molar concentration of hydrogen peroxide caused decrease of the yield of 4,4′-dimethylazoxybenzene and increase of *p*-nitrotoluene, indicating the rapid oxidation from nitroso to nitro compounds in high concentration of hydrogen peroxide. Every sum of the yield of nitrotoluene and 4,4′-dimethylazoxybenzene was less than fifty percent and this may be due to the side reaction such as oxidative cleavage of aromatic portions.

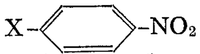
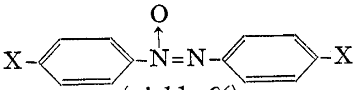
Effect of Substituents on Benzene Ring

The compounds having methyl, chloro, sulfamoyl or nitro group on the *para*-position of N-methylaniline were dissolved in acetic acid using 1450 ml. to one mole of starting material. Hydrogen peroxide oxidation was performed at 100° for seven hours. The yields of nitro compounds and azoxy compounds were shown in Table III.

When the electron-attracting group was located at *para*-position, the yield of the nitro compound decreased and that of azoxy compound increased. The sum of the yields of

Table III. Result of Oxidation of *p*-Substituted N-Methylanilines



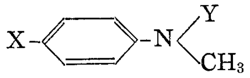
No.	R	H_2O_2 (mole ratio)	 (yield, %)	 (yield, %)
1	CH_3	10	29.6	11.4
2	〃	20	27.3	3.4
3	Cl	10	18.3	34.0
4	〃	20	14.3	35.3
5	SO_2NH_2	10	21.4	45.5
6	〃	20	17.4	36.2
7	NO_2	10	4.4	53.3
8	〃	20	4.3	42.5

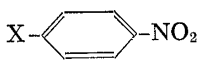
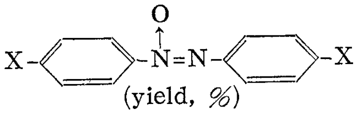
these compounds increased in the case of strong electron-attracting groups as the substituents, indicating stabilization effect of the substituents to the benzene ring.

Effect of Introduction of Acyl Groups on Nitrogen Atoms of N-Alkylanilines

Acyl groups were introduced to nitrogen atoms of N-alkylarylamines in order to inhibit azoxy formation. Acetyl or formyl group was used as the acyl function and either of these was introduced to nitrogen atomes of N-methyl-*p*-toluidine and N-methyl-*p*-nitroaniline. The reaction conditions were the same as employed above. The result was shown in Table IV, comparing with those of N-methylanilines (Nos. 1,2,7, and 8).

Table IV. Result of Oxidation of *p*-Substituted N-Acyl-N-methylanilines



No.	X	Y	H_2O_2 (mole ratio)	 (yield, %)	 (yield, %)
1	CH_3	H	10	29.6	11.4
2	〃	〃	20	27.3	3.4
3	〃	$COCH_3$	10	30.4	0
4	〃	〃	20	31.0	0
5	〃	COH	10	63.8	0
6	〃	〃	20	58.7	0
7	NO_2	H	10	4.4	53.3
8	〃	〃	20	4.3	42.5
9	〃	$COCH_3$	10	43.4	trace
10	〃	〃	20	45.0	0.4

The formation of the azoxy derivatives was scarcely detected in both cases (Nos. 3~6, 9, 10) and further, with the strong electron-attracting group at *para*-position (Nos. 9, 10), the yields of the nitro compounds were remarkable enhanced from the cases of Nos. 7 and 8, where the formation of azoxy compound was predominant.

Based on the mechanism in the case of alkylamino compounds, the oxidation mechanism of acylalkylamino compounds was proposed as follows.

The introduction of formyl group in place of acetyl group caused the increase of the yields of nitro compounds, suggesting that the rates of N-oxidation (I and III) and hydrolysis of acyl group (IV) were made faster by diminishing the sterical hindrance.

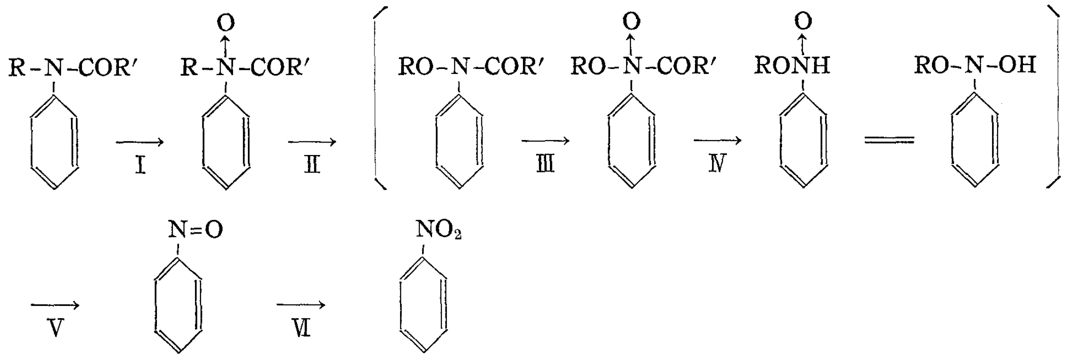


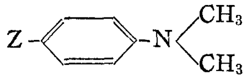
Chart 2.

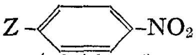
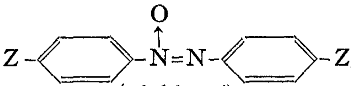
Effect of Introduction of Alkyl Groups on Nitrogen Atoms of N-Alkylanilines

It was expected to get good yields of nitro compounds by further introduction of alkyl group to N-alkylanilines as in the case of introduction of acyl functions, because no formation of azo compound was observed in the reaction between dialkylamino and nitroso compound. The result was shown in Table V.

None of azoxy compounds was obtained as expected, but the yields of nitro compounds were remained very poor. This would be due to the unstable nature of these starting materials against oxidative cleavage of benzene ring.

Table V. Result of Oxidation of *p*-Substituted N,N-Dimethylanilines



No.	Z	H_2O_2 (mole ratio)	 (yield, %)	 (yield, %)
1	CH_3	10	4.2	0
2	〃	20	5.0	0
3	Cl	10	trace	0
4	〃	20	〃	0
5	SO_2NH_2	20	5.4	0
6	〃	30	4.5	0
7	NO_2	15	9.5	0
8	〃	18	12.5	0
9	〃	20	11.9	0
10	〃	25	10.1	0

Based on the mechanism in the case of dialkylamino compounds, a reaction mechanism was proposed as follows.

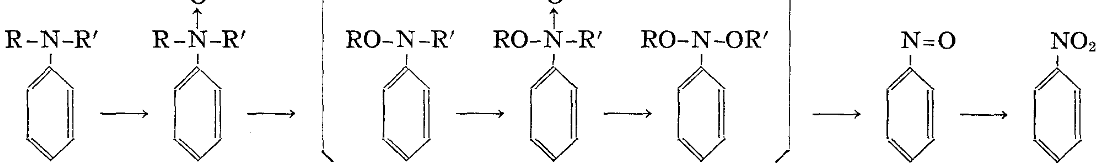


Chart 3.

Experimental[*3]

Oxidation of N-Benzylidene-*p*-toluidine——A mixture of 1 g. of N-benzylidene-*p*-toluidine and 10.5 ml. of 30% H_2O_2 in 7.4 ml. of AcOH was heated on steam bath for 7 hr. The mixture was neutralized with conc. NH_4OH under H_2O cooling, and submitted to steam-distillation. 35 mg. of light yellow crystals, m.p. 50~51°, were obtained as distillate. This substance was identified with *p*-nitrotoluene by mixed melting point determination. From the distillate at the later period, 7 mg. of yellow needles, m.p. 69~70°, was obtained and confirmed to be 4,4′-dimethylazoxybenzene by admixture.

Oxidation of *p*-Isocyanotoluene to *p*-Nitrotoluene——A mixture of 3 g. of *p*-isocyanotoluene and 25.6 ml. of 30% H_2O_2 in 43 ml. of AcOH was heated on a steam bath. After a few minutes, vigorous bubbling occurred and precipitate of a crystalline product was observed in the mixture. After about half hour's heating, the precipitate went into the solution and the mixture became clear. The reaction was continued for 7 hr. The mixture was allowed to cool and neutralized and steam-distilled. 0.79 g. of yellowish crystals of *p*-nitrotoluene, m.p. 49~51°, 22.5% yield; and 0.14 g. of yellow needles of 4,4′-dimethylazoxybenzene were obtained as distillate.

Oxidation of *p*-Isocyanotoluene to 1,3-Ditolylurea——A mixture of 3.2 g. of *p*-isocyanotoluene and 4.2 g. of H_2O_2 in 30 ml. of AcOH was heated on a steam bath for 5 hr. The mixture was evaporated under reduced pressure and the residue was washed with a portion of 50% EtOH. 1.53 g. of colorless scales, m.p. 260~263°, was obtained. Recrystallization of this substance from 50% EtOH gave colorless needles, m.p. 264~265°. No melting point depression was observed when admixed with 1,3-di(*p*-tolyl)urea. *Anal.* Calcd. for $C_{15}H_{16}ON_2$: C, 75.00; H, 6.67; N, 11.67. Found : C, 74.75; H, 6.82; N, 11.58.

Oxidation of 1,3-Di(*p*-tolyl)urea to *p*-Nitrotoluene——A mixture of 2.4 g. of 1,3-di(*p*-tolyl)urea and 7 ml. of 30% H_2O_2 in 14 ml. of AcOH was heated on a steam bath for 6 hr. 0.73 g. of *p*-nitrotoluene was obtained from the mixture by the same treatment as above. Yield 26.3%.

Oxidation of N-Methyl-*p*-toluidine to 4,4′-Dimethylazobenzene——a) A mixture of 2 g. of N-methyl-*p*-toluidine and 13.5 ml. of 30% of H_2O_2 in 20 ml. of AcOH was heated on a steam bath. Vigorous reaction immediately took place and formation of precipitate was detected. After a few minutes, the mixture was cooled and orange crystals, m.p. 125~135° were obtained by filtration of the mixture. This substance was dissolved in benzene and purified through an Al_2O_3 column, and then recrystallized from 80% EtOH to orange needles, m.p. 144~145°, which did not depress with 4,4′-dimethylazoxybenzene. *Anal.* Calcd. for $C_{14}H_{14}N_2$: C, 79.96; H, 6.71; N, 13.32. Found : C, 79.91; H, 6.72; N, 13.20.

b) A mixture of 1 g. of N-methyl-*p*-toluidine and 0.84 ml. of 30% H_2O_2 in 3 ml. of AcOH was allowed to stand for 24 hr. at room temp., To the mixture, 0.5 ml. of 85% HCOOH in 20 ml. of H_2O was added and it was shaken with benzene. The benzene portion was washed with H_2O, dried over Na_2SO_4, and passed over an Al_2O_3 column. 0.21 g. of orange needles, m.p. 136~138°, was obtained. Recrystallization of this substance gave orange needles, m.p. 144~145°. Yield of crude substance, 22.5%.

Formation of 4,4′-Dimethylazobenzene by Condensation of N-Methyl-*p*-toluidine and *p*-Nitrosotoluene——To a solution of 0.1g. of *p*-nitrosotoluene in 1 ml. of petr. ether, was added 0.1 g. of N-methyl-*p*-toluidine. Immediately yellowish turbidity appeared in the mixture. After it was allowed to stand overnight, 0.15 g. of orange needles, m.p. 139~141°, was obtained by concentration of the mixture. Recrystallization of this substance from 80% EtOH gave orange needles, m.p. 144~145°, which were identified as 4,4′-dimethylazobenzene by admixture.

Oxidation of N-Methyl-*p*-toluidine to *p*-Nitrosotoluene——In a 500 ml. distillation flask equipped with a efficient condenser, were placed 5 g. of N-methyl-*p*-toluidine, 29.2 ml. of 30% H_2O_2, 60 ml. of AcOH and 100 ml. of H_2O, and the mixture was heated to boil. When green oily distillate was observed inside of the condenser, 20 ml. of 85% HCOOH and 100 ml. of H_2O were added to the mixture. Then distillation was carried out violently and about 200 ml. of distillate was collected in a 300 ml. flask, in which 40 ml. of Et_2O, 5 ml. of HCOOH and 20 ml. of 20% HCl were placed previously. After shaking, the Et_2O layer was separated and washed with H_2O and dried over Na_2SO_4. 0.6 g. of oily material was obtained by evaporation of the Et_2O solution. 0.1 g. of this substance and 0.15 g. of *p*-aminobenzoic acid were dissolved in 1 ml. of AcOH, the solution was heated on a steam bath for 10 hr. and evaporated under reduced pressure. The residue was dissolved in 10% Na_2CO_3, the Na_2CO_3 solution was acidified with dil. HCl and 0.05 g. of reddish brown precipitate was obtained. This substance was recrystallized from EtOH to orange needles, m.p. 230°(decomp.), which was confirmed to be 4-carboxyl-4′-methylazobenzene by admixture.

Oxidation of N-Methyl-*p*-toluidine to *p*-Nitrotoluene and 4,4′-Dimethylazoxybenzene——A mixture of 2 g. of N-methyl-*p*-toluidine and 13.5 ml. of 30% H_2O_2 in 15.2 ml. of AcOH was heated on a steam bath. The mixture instantly became brown and vigorous boiling took place. Then the mixture was allowed to cool for 30min. and heated again on the steam bath for 6 hr. The mixture was neutralized

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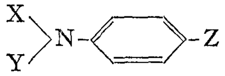
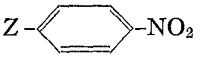
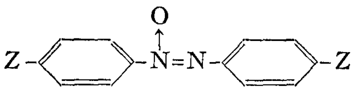
[*3] All melting points were uncorrected.

with conc. NH_4OH under ice-cooling and steam-distilled. 0.5 g. of yellowish crystals, m.p. 50~51.5°, was obtained as distillate (*p*-nitrotoluene*[4]). *Anal.* Calcd. for $C_7H_7O_2N$: N, 10.21. Found : N, 10.31. The mother liquor of steam-distillation was extracted with benzene, the benzene solution was dried over Na_2SO_4 and passed over an Al_2O_3 column. 0.25 g. of yellowish needles, m.p. 68.5~69.5°, was obtained. Recrystallization from 80% EtOH gave yellowish needles melted at 69~70.5°(4,4′-Dimethylazoxybenzene*[4]). *Anal.* Calcd. for $C_{14}H_{14}ON_2$: N, 12.39. Found : N, 12.33.

Oxidation of N-Methyl-*p*-chloroaniline to *p*-Nitrochlorobenzene and 4,4′-Dichloroazoxybenzene——A mixture of 1 g. of N-methyl-*p*-chloroaniline and 7.2 ml. of 30% H_2O_2 in 9.8 ml. of AcOH was heated on a steam bath for 7 hr. The mixture was neutralized with conc. NH_4OH under cooling and steam-distilled. 0.201 g. of yellowish needles, m.p. 79~81°, was obtained as distillate. Recrystallization of this substance from aq. EtOH gave colorless needles, m.p. 81~82° (*p*-nitrochlorobenzene*[4]). *Anal.* Calcd. for $C_6H_4O_2NCl$: C, 45.71; H, 2.54; N, 8.89. Found : C, 45.65; H, 2.63; N, 8.78. From the mother liquor of steam-distillation, 0.332 g. of orange scales, m.p. 152~154°, was obtained by filtration. Recrystallization of this substance from aq. EtOH afforded orange needles, m.p. 155~156° (4,4′-dichloroazoxybenzene*[4]). *Anal.* Calcd. for $C_{12}H_8ON_2Cl$: C, 53.93; H, 3.00; N, 10.49. Found : C, 53.96; H, 3.19; N, 10.66.

Oxidation of N⁴-Methylsulfanilamide to *p*-Nitrobenzenesulfonamide and 4,4′-Disulfamoylazoxybenzene——A mixture of 1 g. of N^4-methylsulfanilamide and 5.5 ml. of 30% H_2O_2 in 7.3 ml. of AcOH was heated

TABLE VI.


X	Y	Z	30% H_2O_2		AcOH				
			(ml.)	(mole ratio)	(ml.)	(mg.)	(%)	(mg.)	(%)
CH_3	H	CH_3	6.8	8	18.0	250	22.0	125	13.4
〃	〃	〃	10.1	12	11.9	330	29.0	60	6.4
〃	〃	〃	15.2	18	17.9	402	35.4	46	4.9
〃	〃	〃	8.4	10	11.9	335	29.6	107	11.4
〃	〃	〃	16.8	20	11.9	309	27.3	32	3.4
C_2H_5	〃	〃	9.1	12	10.8	214	21.1	40	4.8
〃	〃	〃	13.6	18	16.2	260	25.6	26	3.1
C_3H_7	〃	〃	8.2	12	9.8	169	18.4	49	6.5
〃	〃	〃	12.3	18	14.3	228	24.8	32	4.2
CH_3	〃	Cl	7.2	10	9.8	201	18.3	322	34.0
〃	〃	〃	14.4	20	9.8	156	14.3	333	35.3
〃	〃	SO_2NH_2	5.5	10	7.3	197	21.4	426	45.5
〃	〃	〃	11.0	20	7.3	160	17.4	347	36.2
〃	〃	NO_2	6.7	10	8.3	48	4.4	505	53.3
〃	〃	〃	13.4	20	8.3	47	4.3	402	42.5
〃	$COCH_3$	CH_3	6.3	10	8.9	255	30.4	0	0
〃	〃	〃	12.5	20	8.9	260	31.0	0	0
〃	COH	〃	6.8	10	9.7	586	63.8	0	0
〃	〃	〃	13.7	20	9.7	540	58.7	0	0
〃	$COCH_3$	NO_2	5.3	10	7.4	376	43.4	—	trace
〃	〃	〃	10.5	20	7.4	390	45.0	3	0.4
〃	CH_3	CH_3	7.6	10	10.6	43	4.2	0	0
〃	〃	〃	15.1	20	10.6	51	5.0	0	0
〃	〃	Cl	6.6	10	8.6	—	trace	0	0
〃	〃	〃	13.1	20	8.6	—	〃	0	0
〃	〃	SO_2NH_2	10.2	20	7.2	54	5.4	0	0
〃	〃	〃	15.6	30	7.2	45	4.5	0	0
〃	〃	NO_2	9.2	15	8.1	96	9.5	0	0
〃	〃	〃	11.1	18	8.1	127	12.5	0	0
〃	〃	〃	12.3	20	8.1	120	11.9	0	0
〃	〃	〃	15.3	25	8.1	102	10.1	0	0

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*[4] Confirmed by admixture.

on a steam bath. Color of the mixture immediately turned brown and a large amount of scales precipitated. The reaction was continued for 7 hr., and the mixture was cooled with ice H_2O. Yellowish orange needles came out and they were collected by filtration. 0.426 g., m.p. 288~289° (4,4′-disulfamoylazoxybenzene*[4]). *Anal.* Calcd. for $C_{12}H_{12}O_5N_4S_2$: C, 40.45; H, 3.40; N, 15.73. Found : C, 40.33; H, 3.43; N, 15.57. The mother liquor of filtration was evaporated to dryness under reduced pressure and the residue was treated with 3 ml. of 2*N* HCl. 0.197 g. of yellow prisms, m.p. 162~171°, gradually precipitated. These were recrystallized from H_2O to yellowish prisms, m.p. 175~176° (*p*-nitrobenzenesulfonamide*[4]). *Anal.* Calcd. for $C_6H_6O_4NS$: C, 35.65; H, 2.99; N. 13.86. Found : C, 35.43; H, 2.98; N, 13.92.

Oxidation of N-Methyl-*p*-nitroaniline to 1,4-Dinitrobenzene and 4,4′-Dinitroazoxybenzene——A mixture of 1 g. of N-methyl-*p*-nitroaniline and 6.7 ml. of 30% H_2O_2 in 8.3 ml. of AcOH was heated on a steam bath for 7 hr. After neutralization with conc. NH_4OH, the mixture was steam-distilled. 0.048 g. of needles, m.p. 170~171° was obtained as distillate. This was recrystallized from EtOH to colorless needles, m.p. 171~172° (*p*-dinitrobenzene*[4]). *Anal.* Calcd. for $C_6H_4O_4N_2$: C, 42.86; H, 2.40. Found : C, 42.91; H, 2.96. From the mother liquor of steam-distillation, 0.505 g. of brownish yellow scales, m.p. 175~185°, was obtained as precipitate. This was recrystallized from EtOH to yellow needles, m.p. 178~185° (4,4′-dinitroazoxybenzene*[4]). *Anal.* Calcd. for $C_{12}H_8O_5N_2$: C, 50.01; H, 2.80. Found : C, 50.00; H, 2.92.

Summary of the Results of Oxidation of *p*-Substituted N-Alkylamines——The results of oxidations of *p*-substituted N-alkylamines were summarized in Table Ⅵ (1 g. of the starting material was employed in each oxidation).

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Summary

Various aromatic nitrogen compounds were oxidized with hydrogen peroxide and it was found that derivatives of alkylarylamines were oxidized to corresponding nitro compounds in good yields. The mechanism of the oxidation to nitro compound was deduced. The effects of substituents in benzene ring and of acyl functions on amino nitrogen atoms were investigated. N-Acyl, especially N-formyl derivatives of alkylarylamines were shown to give the best results to afford nitro compounds.

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