The precipitate, m.p. 174~177°, was recrystallized from H_2O to yellowish needles (m.p. 177~178°), which was undepressed on admixture with 4-nitrobenzenesulfonamide. The yields corresponding to various conditions, were shown below.

Formation of *p*-Nitrosotoluene by Oxidation of 4′-Methylacetanilide——A mixture of 4′-methylacetanilide (5 g.) and 30% H_2O_2 (28ml.) in AcOH (48 ml.) was heated on a steam bath for 0.5 hr., and then neutralized with conc. NH_4OH under ice-cooling. 85% HCOOH (15 ml.) was added and the solution was submitted to steam-distillation, the distillate was extracted with Et_2O and the Et_2O solution was dried (Na_2SO_4) and evaporated to dryness, 0.8 g. of a green oily material was obtained. A mixture of this substance (0.2 g.) and *p*-aminobenzoic acid (3.0 g.) in AcOH (2 ml.) was heated on a steam bath for 10 hr., and it was evaporated *in vacuo* to dryness, the residue was dissolved in 10% Na_2CO_3 and the Na_2CO_3 solution was acidified with dil. HCl. Reddish brown precipitate (0.05 g.) was collected by filtration. This substance was recrystallized from EtOH to orange needles, m.p. 283°(decomp.), which was undepressed with *p*-(*p*-tolylazo)benzoic acid, IR spectra of both substances were superimposable. *Anal.* Calcd. for $C_{14}H_{12}O_3N_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.76; H, 5.08; N, 11.54.

Formation of *p*-Nitrotoluene by Oxidation of *p*-Nitrosotoluene——A mixture of *p*-nitrosotoluene (0.17 g.) and 30% H_2O_2 (0.6 ml.) in AcOH (2.5 ml.) was heated on a steam bath for 1 hr. The mixture was neutralized with conc. NH_4OH under ice-cooling and submitted to steam-distillation, yellowish needles (0.16 g.) m.p. 50~51°, was obtained as distillate. This substance was identified as *p*-nitrotoluene by admixture.

The author expresses his deep gratitude to Prof. Emeritus E. Ochiai and Prof. T. Okamoto of the University of Tokyo for kind guidance, to Prof. T. Kosuge of Shizuoka College of Pharmacy for valuable advice, to President T. Owada, Vice-President T. Tanaka, Managing Director K. Oga, Director T. Sakata and Dr. H. Okeda of Nippon Soda Co., Ltd. for helpful encouragement. He is also indebted to Miss. E. Ishiguro for assistance, to Miss Y. Saito for elemental analyses.

Summary

A new reaction mechanism of the oxidation of acylamino compounds by hydrogen peroxide to afford nitro compounds was proposed.

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48. **Haruyuki Ito**: Synthesis of Nitro Compounds by Means of Oxidation of Acylamino Compounds. X[*1]. Reinvestigation of Reaction Conditions of Oxidation of Acylamino Compounds to Nitro Compounds.

(*Shizuoka College of Pharmacy*[*2])

In the Part Ⅸ[*1] of this series, a suggestion of the new mechanism has been made for the oxidation of acylamino compounds to nitro compounds by means of hydrogen peroxide in glacial acetic acid. Based on this mechanism, it was considered that the introduction of electron-releasing groups to the benzene nucleus would increase the yields of the resulting nitro compounds and electron-attracting groups, on the other hand, would decrease the formation of the nitro compounds. However, the opposite experimental results to this consideration have been reported in the previous paper[1] and therefore, it was necessary to explain the reasons of this disagreement. This paper

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[*1] Part Ⅸ: This Bulletin, **12**, 326 (1964).

[*2] Oshika, Shizuoka (伊藤晴之).

[1] T. Kosuge, *et al.*: Kenkyu Nenpo (Faculty of Pharm., Univ. of Kanazawa), **2**, 22 (1952).

mainly concerns to this subject as well as the re-investigations about the reaction conditions of the hydrogen peroxide oxidation *versus* various kinds of substituted acylamino compounds, and the results were discussed in the relation with the effect of both substituents and acyl groups to the yields of nitro compounds and azoxy compounds.

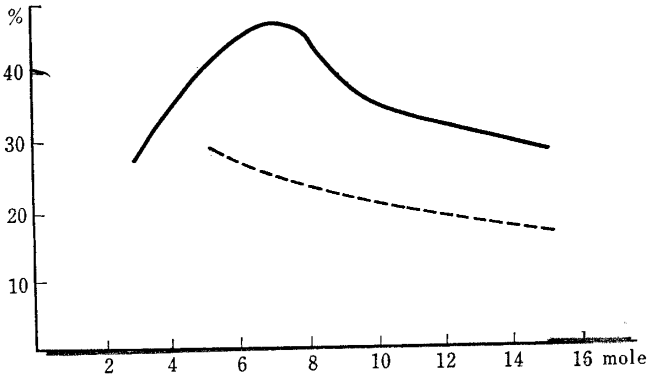
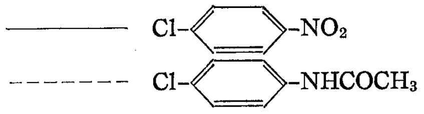


Fig. 1. Effects of the Amount of Hydrogen Peroxide in the Oxidation of 4′-Chloroacetanilide



I. Effect of the Amount of Hydrogen Peroxide

The hydrogen peroxide oxidation of five acylamino compounds, *i.e.* 3′-(and 4′)-chloroacetanilide, 4′-methoxyacetanilide, 4′-chloroformanilide, 4′-methoxyformanilide was studied with varied amounts of the oxidation reagent and the yields of nitro and azoxy compounds, the amounts of the recovered acylamino compounds were plotted against the amount of hydrogen peroxide employed (Figs. 1~5). The reaction was carried out at 100° for seven hours in glacial acetic acid and 1450 ml. of the solvent was used to one mole of the starting acylamino compounds.

i) About the Results of Oxidation of Acetanilides

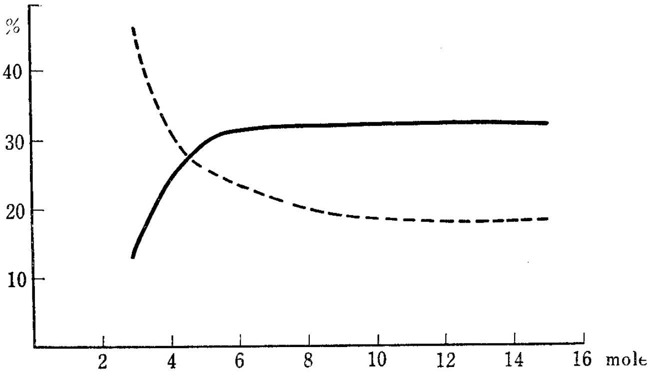
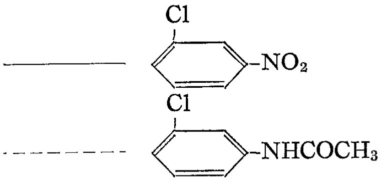


Fig. 2. Effects of the Amount of Hydrogen Peroxide in the Oxidation of 3′-Chloroacetanilide



In the cases of *p*- and *m*-substituted acetanilides with the electron-attracting group (Figs. 1 and 2), the corresponding nitro compounds were obtained in relatively good yields and the starting materials were recovered even at large amount of hydrogen peroxide. Contrarily, the introduction of the electron-releasing group (Fig. 3) reduced the yield, and the recovery was observed only when the small amount of hydrogen peroxide was employed. Two possible side reactions were conceivable, which affected the yield of the nitro compounds and those were reported to be the oxidative cleavage of the benzene nuclei and the formation of azoxy compounds.[2] Since no formation of azoxy compounds was detected, the decrease of the yield would be attributable to the side reaction of oxidative cleavage. This agreed well with the fact that the amount of the recovered starting material decreased by introduction of the electron-releasing group which increased the reactivity of the benzene ring, and contrariwise the increase of the recovery was observed by

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[2] T. Kosuge, S. Miyashita : Yakugaku Zasshi, **74**, 1381 (1954).

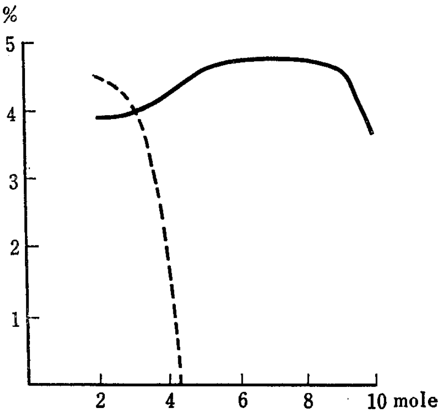
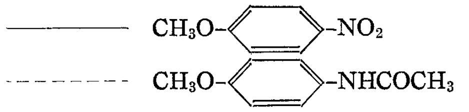


Fig. 3. Effects of the Amount of Hydrogen Peroxide in the Oxidation of 4′-Methoxyacetanilide



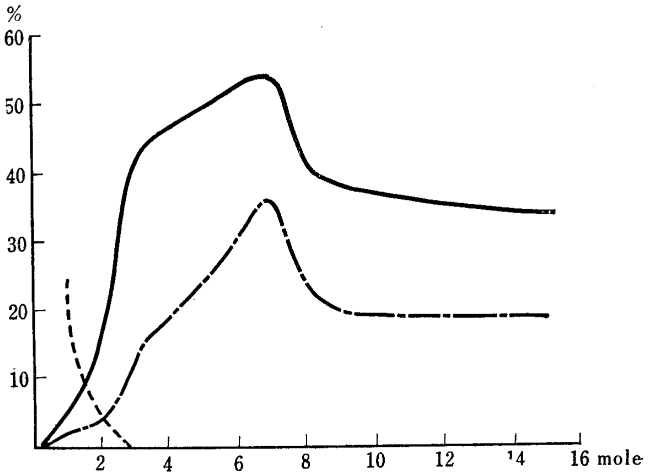
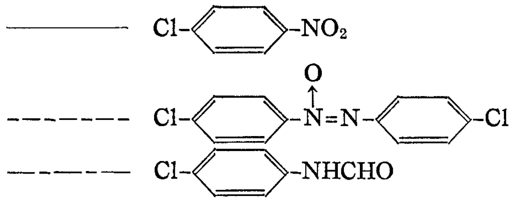


Fig. 4. Effects of the Amount of Hydrogen Peroxide in the Oxidation of 4′-Chloroformanilide



introduction of the electron-attracting group which increased the stability of the benzene nucleus.

In the case of 4′-chloroacetanilide (Fig. 1), the maximum yield (47%) of *p*-nitrochlorobenzene was observed with seven moles of hydrogen peroxide, whereas the formation of *m*-nitrochlorobenzene (Fig. 2) reached to 33% with seven moles of the reagent and the increased amount of hydrogen peroxide scarcely affected the yield of the nitro compound. Curves of the recovered acetanilides were analogous in both cases. From these results, it was deduced that 4′-chloroacetanilide was oxidized a little more readily than the *meta* derivative and the nitro compound from the latter was more stable than *p*-nitro chlorobenzene.

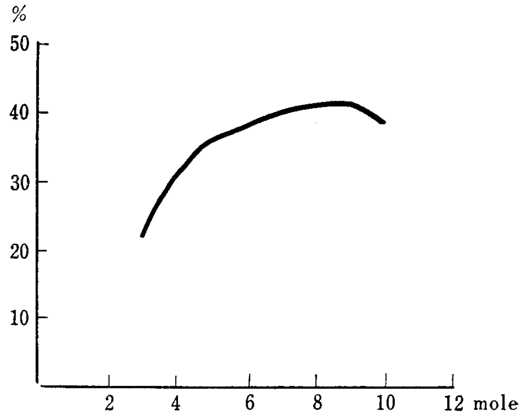
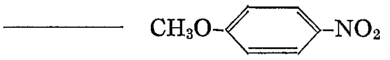


Fig. 5. Effects of the Amount of Hydrogen Peroxide in the Oxidation of 4′-Methoxyformanilide



ii) Effects of Acyl Group

When the formyl group was employed as an acyl group of *p*-substituted acylaniline (Figs. 4 and 5), it was found that the yields of the resulting nitro compounds were considerably enhanced compared with corresponding acetyl compounds and this phenomenon was characteristic to a formanilide with the electron releasing group (Fig. 5). From the comparisons of both dissociation constant[*3] of formic acid and the rate of acid

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[*3] International Critical Table, **6**, 261 (1933).

Substance	Temp. (°C)	Conc. (mole/L.)	Const. of dissociation
HCOOH	15	0.25~0.001	2.0×10^{-4}
〃	25	0.12~0.001	2.1×10^{-4}
CH_3COOH	15	0.08~0.001	1.806×10^{-5}
〃	25	0.06~0.005	1.813×10^{-5}

saponification*[4] of formic esters with those of acetic acid and its esters, it would be deduce that the formyl group would be more electronegative than the acetyl group. However, Kosuge has reported in the previous paper[1)] of this series, that the yields of nitro compounds extremely decrease when benzoyl or *p*-nitrobenzoyl group is introduced as an acyl group of acylamine compounds. As these acyl groups are discussed[1)] to be more electronegative than acetyl group, enhanced yields of oxidation products in the case of formylamine may be ascribed to the small steric hindrance of the fromyl group, which facilitates the N-oxidation with hydrogen peroxide.

An azoxy compound was found to be another reaction product in the case of 4′-chloroformanilide (Fig. 4), although no azoxy formation was discernible in Fig. 1. Since the formyl group is more electronegative than the acetyl group, a part of formamide and or formamide N-oxide would be hydrolized in this oxidation condition to amino and/or hydroxylamino compounds, which are condensed with the nitroso compound, an intermediate of this oxidation,*[1] to form azo and/or azoxy compounds, the former being oxidized further to the latter.[2),3)] The maximum yield (36%) of the azoxy compound in Fig. 4 corresponds to that of the nitro compound at seven moles of hydrogen peroxide and the sum of the yields of azoxy and nitro compounds is almost theoretical (91%). Decrease of the yields of both compounds at higher cleavage of the benzene portion.

In the case of the formylamino compound with electron-releasing group (Fig. 5), no azoxy compound was detected and this would be reasoned by the effect of the substituent which strengthened the N-C bond of the formyl amine group.

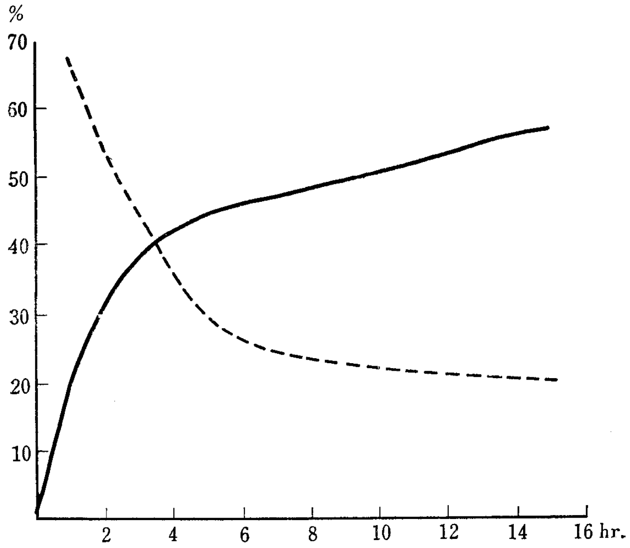
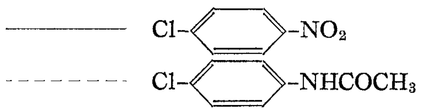


Fig. 6. Effects of Reaction Time in the Oxidation of 4′-Chloroacetanilide



II. Effects of Reaction Time

In the oxidation of three compounds, *i.e.* 4′-chloroacetanilide, 4′-methoxyacetanilide and 4′-methoxyformanilide, the yields of nitro compounds and the amount of recovery of acylamino compounds were studied in relation to the reaction time. The reaction condition was selected to be optimal and the oxidation was carried out by heating at 100° for the given time with seven moles (Fig. 6) or nine moles (Figs. 7 and 8) of 30% hydrogen peroxide in glacial acetic acid, whose amount was at the ratio of 1450 ml. to one mole of starting materials. The results were shown in Figs. 6~8.

In the case of introduction of the electron-attracting group (Fig. 6), the yield of the nitro compound increased

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*[4] International Critical Table, **7**, 133 (1933).

Substance	Temp. (°C)	Rate const. of acid saponification
$HCOOCH_3$	25	0.145
$HCOOC_2H_5$	25	0.187
CH_3COOCH_3	25	0.00680
$CH_3COOC_2H_5$	25	0.00658

3) E. Bamberger, *et al.* : Ber., **31**, 1522 (1898); **32**, 342, 1675, 1882 (1899); Ann., **311**, 78 (1900).

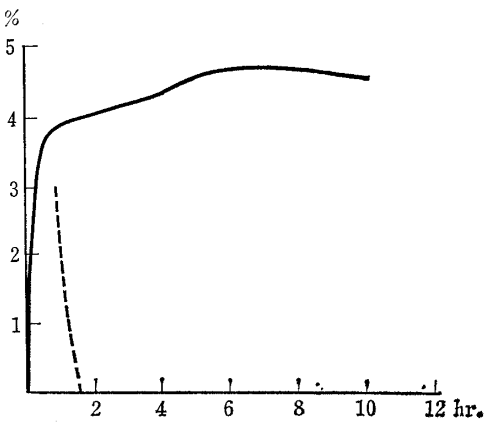
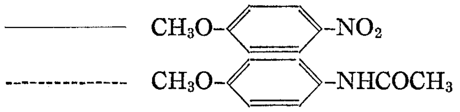


Fig. 7. Effects of Reaction Time in the Oxidation of 4′-Methoxyacetanilide



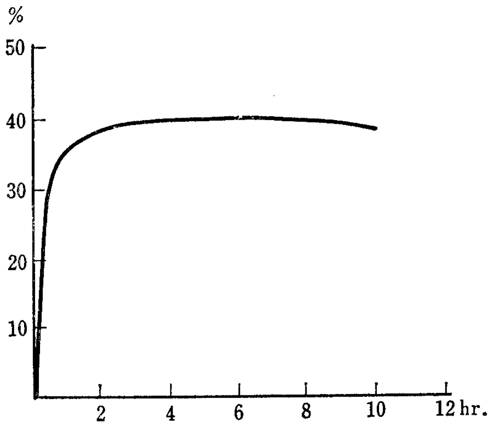
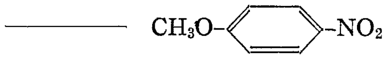


Fig. 8. Effects of Reaction Time in the Oxidation of 4′-Methoxyformanilide



gradually and the recovery decreased with the prolonged reaction time and the total yield of the nitro compound and the recovery after five hours was nearly constant. This fact exhibits that the oxidation proceeds gradually and the oxidative decomposition scarcely takes place even after prolonged heating.

In the case of electron-releasing group (Fig. 7 and 8), the recovery was observed at the earlystage only in the case of acetylamine. This indicates that the N-oxidation of starting materials proceeds very rapidly and the decomposition of nitro compounds occurs at the several hour's heating.

By comparing the recovery curves of the starting materials in Fig. 6~8, it is assumed that the rate of N-oxidation of acylamines is at the order of 4′-methoxyformanilide>4′-methoxyacetanilide>4′-chloroacetanilide.

III. Effect of the Amount of Glacial Acetic Acid

In the oxidation of three compounds, *i.e.* 4′-chloroacetanilide, 3′-chloroacetanilide, and 4′-chloroformanilide the yields of nitro and azoxy compounds and the amount of the recovery of acylamino compounds were studied in relation to the amount of glacial acetic acid. The reaction was carried out by heating at 100° with seven moles of 30% hydrogen peroxide for seven hours in various amounts of acetic acid and the results were shown in Figs. 9~11.

In the oxidation of 4′-chloroacetanilide (Fig. 9), the yield of the nitro compound increased gradually with the increase of the amount of acetic acid whereas the recovery

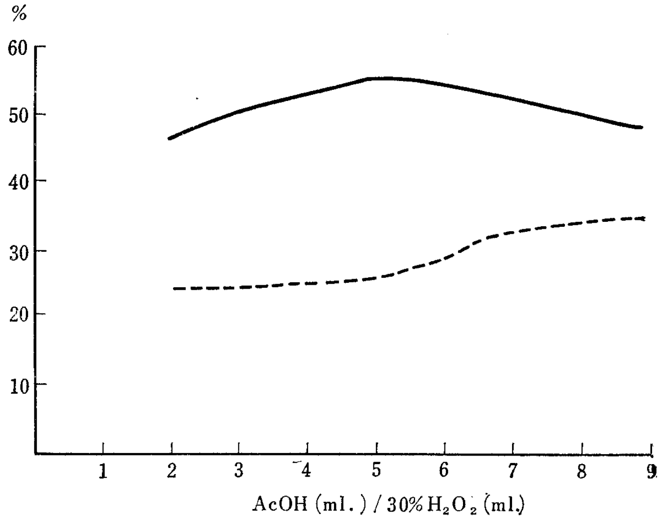
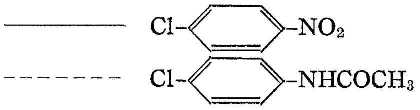


Fig. 9. Effects of the Amount of Glacial Acetic Acid in the Oxidation of 4′-Chloroacetanilide



was unaffected until five volume ratio of the solvent *versus* 30% hydrogen peroxide, but over this point, the former decreased and the latter gradually increased. This indicates that the increase of the amount of acetic acid contributes to the increase of the yield of nitro compound through retardation of oxidative decomposition, but the further increase of the solvent over some extent decreases the rate of N-oxidation at the acetylamino group.

In the case of 4′-chloroacetanilide (Fig. 11), rate of N-oxidation to the formylamino group is fast enough and it is much unaffected by dilution.

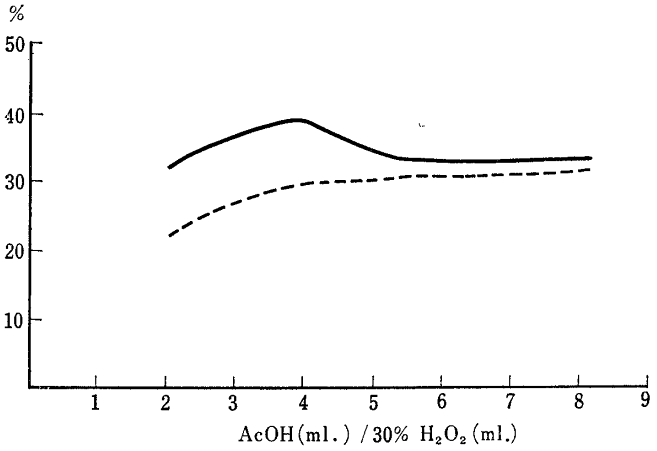
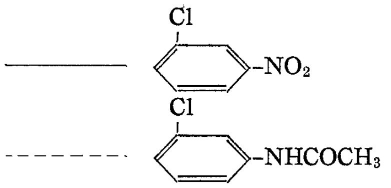


Fig. 10. Effects of the Amount of Glacial Acetic Acid in the Oxidation of 3′-Chloroacetanilide



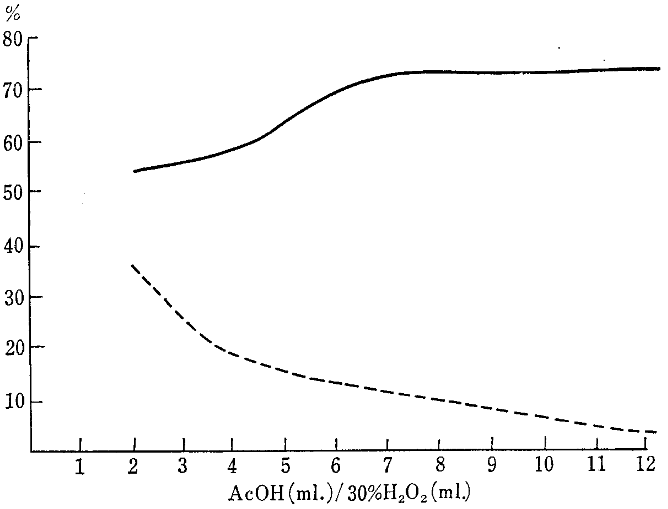
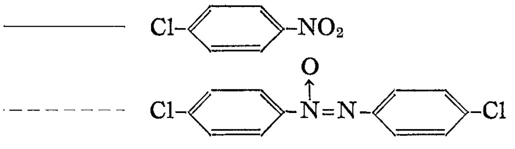


Fig. 11. Effects of the Amount of Glacial Acetic Acid in the Oxidation of 4′-Chloroformanilide

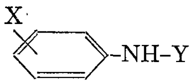
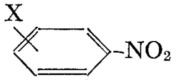
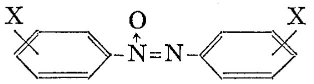
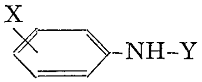


Experimental

Oxidation of Acetanilides to Nitrobenzenes——Acylamino compounds (1/50 mole) were oxidized at the varied conditions as shown in Table I. After cooling, the reaction mixture was neutralized with conc. NH_4OH under ice-cooling. The neutralized mixture was steam-distilled, crystals in distillate were collected by filtration and were confirmed to be the corresponding nitro compound by mixed melting points with the known sample. When the precipitate was observed in the remaining solution of steam-distillation, it was gathered by filtration. This was examined by mixed melting points whether it was identical with the starting material or not. When the melting point depression was observed, it was hydrolized with 5 ml. of 10% HCl on a steam bath for 1 hr., and the azoxy compound was obtained as the insoluble precipitate, which was confirmed by mixed melting points with the known sample. In the case of *m*-acetylaminochlorobenzene, the precipitate in the remaining solution of steam-distillation was oily material, so that, the recovery of starting meterial was performed by Al_2O_3 column chromatography after extraction with benzene. The results were summarized in Table I.

The author expresses his deep gratitude to Prof. Emeritus E. Ochiai and Prof. T. Okamoto of the University of Tokyo for their kind guidances, to Prof. T. Kosuge of Shizuoka College of Pharmacy for his valuable advices, to President T. Owada, Vice-President T. Tanaka, Managing Director K. Oga, Director Dr. T. Sakata and Dr. H. Okeda of Nippon Soda Co., Ltd. for helpful encouragement. He is also indebted to Miss S. Tatsumi and S. Okada for assistance.

Table I. Results of Oxidation of *para* or *meta* Substituted Acylanilines in Varied Conditions

Materials			Oxidizing reagent		Solvent		Temp.	Time	Product		By-products		Recovery	
			30% H_2O_2		AcOH									
X	Y	(g.)	(ml.)	(mole ratio)	(ml.)	(ml./H_2O_2 ml.)	(°C)	(hr.)	(g.)	(%)	(g.)	(%)	(g.)	(%)
p-Cl	$COCH_3$	3.4	6.1	3	29	4.75	100	7	0.87	27.6	0	0	—	—
〃	〃	3.4	10.2	5	29	2.85	100	7	1.26	40.0	0	0	1.01	29.6
〃	〃	3.4	14.3	7	29	2.03	100	7	1.48	47.1	0	0	0.84	24.7
〃	〃	3.4	16.3	8	29	1.78	100	7	1.43	45.5	0	0	0.80	23.5
〃	〃	3.4	18.4	9	29	1.58	100	7	1.23	38.9	0	0	0.75	22.1
〃	〃	3.4	30.6	15	29	0.94	100	7	0.88	27.9	0	0	0.54	15.9
m-Cl	〃	3.4	6.1	3	29	4.75	100	7	0.34	12.7	0	0	1.56	45.9
〃	〃	3.4	10.2	5	29	2.85	100	7	0.92	29.2	0	0	0.89	26.2
〃	〃	3.4	14.3	7	29	2.03	100	7	1.01	32.1	0	0	0.75	22.1
〃	〃	3.4	18.4	9	29	1.58	100	7	1.00	31.7	0	0	0.67	19.7
〃	〃	3.4	30.6	15	29	0.94	100	7	1.00	31.7	0	0	0.62	18.2
p-OCH_3	〃	3.3	4.0	2	29	7.25	100	7	0.12	3.9	0	0	0.15	4.5
〃	〃	3.3	6.1	3	29	4.75	100	7	0.12	3.9	0	0	0.14	4.2
〃	〃	3.3	8.2	4	29	3.54	100	7	0.13	4.2	0	0	0.05	1.5
〃	〃	3.3	10.2	5	29	2.85	100	7	0.14	4.6	0	0	0	0
〃	〃	3.3	14.3	7	29	2.03	100	7	0.15	4.7	0	0	0	0
〃	〃	3.3	16.3	8	29	1.78	100	7	0.15	4.7	0	0	0	0
〃	〃	3.3	18.4	9	29	1.58	100	7	0.15	4.7	0	0	0	0
〃	〃	3.3	20.4	10	29	1.42	100	7	0.11	3.6	0	0	0	0
p-Cl	COH	3.1	2.0	1	29	14.50	100	7	0.16	5.2	0.07	2.6	0.81	23.8
〃	〃	3.1	4.0	2	29	7.25	100	7	0.54	17.1	0.12	4.4	0.21	3.5
〃	〃	3.1	6.1	3	29	4.75	100	7	1.30	41.3	0.40	14.8	0	0
〃	〃	3.1	10.2	5	29	2.85	100	7	1.58	50.2	0.66	24.8	0	0
〃	〃	3.1	14.3	7	29	2.03	100	7	1.70	54.0	0.96	36.0	0	0
〃	〃	3.1	16.3	8	29	1.78	100	7	1.26	40.0	0.64	22.0	0	0
〃	〃	3.1	18.4	9	29	1.58	100	7	1.21	38.4	0.54	20.2	0	0
〃	〃	3.1	30.6	15	29	0.94	100	7	1.08	34.3	0.50	18.7	0	0
p-OCH_3	〃		6.1	3	29	4.75	100	7	0.83	21.1	0	0	0	0
〃	〃	3.1	10.2	5	29	2.85	100	7	1.12	36.3	0	0	0	0
〃	〃	3.1	12.2	6	29	2.46	100	7	1.18	38.5	0	0	0	0

〃	〃	3.1	16.3	8	29	1.78	100	7	1.23	40.2	0	0	0	0
〃	〃	3.1	18.3	9	29	1.58	100	7	1.26	41.2	0	0	0	0
〃	〃	3.1	20.3	10	29	1.42	100	7	1.13	37.8	0	0	0	0
p-Cl	$COCH_3$	3.4	14.3	7	29	2.03	100	1	0.62	19.7	0	0	2.28	67.1
〃	〃	3.4	14.3	7	29	2.03	100	3	1.20	38.1	0	0	1.54	45.3
〃	〃	3.4	14.3	7	29	2.03	100	5	1.40	44.4	0	0	1.00	29.3
〃	〃	3.4	14.3	7	29	2.03	100	7	1.48	47.1	0	0	0.84	24.7
〃	〃	3.4	14.3	7	29	2.03	100	9	1.66	50.2	0	0	0.76	22.4
〃	〃	3.4	14.3	7	29	2.03	100	15	1.76	55.9	0	0	0.68	20.0
m-Cl	〃	3.4	14.3	7	29	2.03	100	1	0.61	19.0	0	0	1.43	42.1
〃	〃	3.4	14.3	7	29	2.03	100	3	1.01	32.1	0	0	1.26	37.1
〃	〃	3.4	14.3	7	29	2.03	100	5	1.01	32.1	0	0	0.76	22.4
〃	〃	3.4	14.3	7	29	2.03	100	7	1.01	32.1	0	0	0.75	22.1
〃	〃	3.4	14.3	7	29	2.03	100	15	0.96	30.5	0	0	0.58	17.1
p-OCH_3	〃	3.3	18.4	9	29	1.58	100	1	0.12	3.9	0	0	0.10	3.0
〃	〃	3.3	18.4	9	29	1.58	100	3	0.13	4.2	0	0	0	0
〃	〃	3.3	18.4	9	29	1.58	100	5	0.14	4.6	0	0	0	0
〃	〃	3.3	18.4	9	29	1.58	100	7	0.15	4.7	0	0	0	0
〃	〃	3.3	18.4	9	29	1.58	100	10	0.14	4.6	0	0	0	0
〃	COH	3.0	18.4	9	29	1.58	100	1	1.20	35.9	0	0	0	0
〃	〃	3.0	18.4	9	29	1.58	100	3	1.23	40.2	0	0	0	0
〃	〃	3.0	18.4	9	29	1.58	100	5	1.24	40.5	0	0	0	0
〃	〃	3.0	18.4	9	29	1.58	100	7	1.26	41.2	0	0	0	0
〃	〃	3.0	18.4	9	29	1.58	100	10	1.22	39.5	0	0	0	0
p-Cl	$COCH_3$	3.4	14.3	7	29	2.03	100	7	1.48	47.0	0	0	0.84	24.7
〃	〃	3.4	14.3	7	58	4.06	100	7	1.68	53.3	0	0	0.86	25.3
〃	〃	3.4	14.3	7	73	5.10	100	7	1.80	55.0	0	0	0.86	26.2
〃	〃	3.4	14.3	7	97	6.78	100	7	1.65	52.4	0	0	1.09	32.1
〃	〃	3.4	14.3	7	126	8.80	100	7	1.52	48.2	0	0	1.17	34.4
m-Cl	〃	3.4	14.3	7	29	2.03	100	7	1.01	32.1	0	0	0.75	22.1
〃	〃	3.4	14.3	7	58	4.06	100	7	1.22	38.7	0	0	1.00	29.4
〃	〃	3.4	14.3	7	73	5.10	100	7	1.05	33.3	0	0	--	—
〃	〃	3.4	14.3	7	116	8.11	100	7	1.05	33.3	0	0	1.09	32.1
p-Cl	COH	3.1	14.3	7	29	2.03	100	7	1.70	54.0	0.96	36.0	0	0
〃	〃	3.1	14.3	7	58	4.06	100	7	1.83	58.1	0.47	17.6	0	0
〃	〃	3.1	14.3	7	87	6.08	100	7	2.23	70.8	0.36	13.4	0	0
〃	〃	3.1	14.3	7	174	12.18	100	7	2.35	74.6	0.10	3.6	0	0

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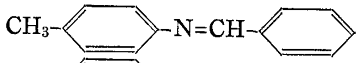
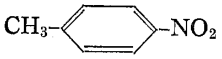
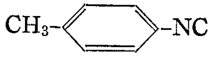
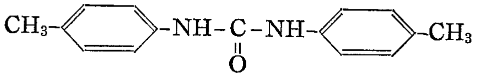
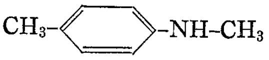
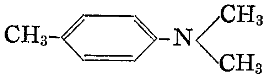
49. **Haruyuki Ito** : Synthesis of Nitro Compounds by Means of Oxidation of Acylamino Compounds. XI.[*1] Oxidation of Alkylamino Compounds with Hydrogen Peroxide.

(*Shizuoka College of Pharmacy*[*2])

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).