Preparation of Linear Oligoaniline Derivatives Using Titanium Alkoxide as a Condensing Agent[1)]

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Synopsis. Linear oligoaniline derivatives were prepared by the reaction of aromatic amines and phenols using various titanium alkoxides as condensing agents. The oligomers obtained were silver white microscopic crystals. Titanium alkoxides used were titanium alkoxide or titanium alkoxide aryloxide and the latter showed high dehydration condensation activity in comparison with the usual titanium alkoxides.

Polyaniline derivatives have been widely investigated because of their electroactive properties. Such polymers are usually prepared by electropolymerization[2—4)] and are not single substances but a mixture of nigroaniline, emeraldine, and other components. Moreover, their molecular weights or numbers of aromatic rings cannot be measured. On the other hand, J. Honzl et al.[5,6)] prepared some linear oligoaniline derivatives as a model polymer. The derivatives were prepared by the reaction of diethyl esters of terephthalic acid and aromatic amines as starting materials. But this method requires complicated operations and high vacuums for sublimation and deamination, and even-numbered analogues such as hexamer and octamer cannot be obtained. In USP,[7)] there has been reported the preparation of secondary aromatic amines by the reaction of primary aromatic amines and phenols using titanium alkoxides as condensing agents. But this reaction has to be done at an elevated temperature under reflux conditions in an autoclave. Furthermore, the yield of the product is not satisfactorily high.

We investigated the synthesis of linear oligoanilines under mild conditions in benzene or toluene as solvent at atmospheric pressure by the reaction of aromatic amines and phenols using titanium alkoxides as condensing agents. Linear oligoaniline derivatives, especially, α-phenyl-ω-hydrotetra(imino-*p*-phenylene) (abbreviated to *N*-phenyltetraaniline, hereafter), α-phenyl-ω-hydropenta(imino-*p*-phenylene) (*N*-phenylpentaaniline, hereafter), and α-*p*-aminophenyl-ω-hydrotetra(imino-*p*-phenylene) (*N*-*p*-aminophenyltetraaniline, hereafter) were obtained in high yield using titanium alkoxide aryloxides.

Experimental

Melting points were measured in a sealed tube with Mitamura Riken Kogyo Mel-Temp and were uncorrected. All procedures were done under a nitrogen atmosphere. The synthesized oligoanilines were identified by elemental analysis and IR and MS spectral analyses.

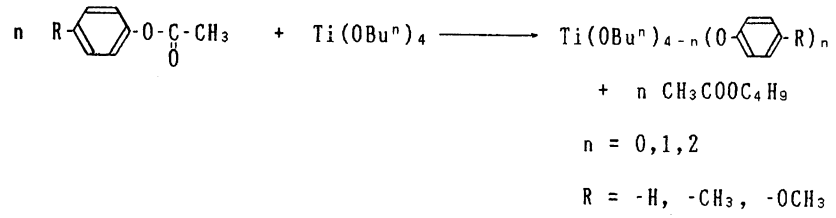
Preparation of Titanium Tributoxide Phenoxide: Titanium tetrabutoxide (34.03 g) (TBT) and phenyl acetate (133.62 g) were put into a reaction flask, and butyl acetate was distilled out from the reaction mixture, leaving an yellowish product in the bottom of the flask.

Preparation of *N*-Phenyltetraaniline (1): Benzene (50 ml) and *p*-phenylenediamine (0.54 g) were put into a reaction flask and the reaction temperature was kept at 70 °C. Then titanium tetraisopropoxide (8.52 g) (TPT) was added to the reaction flask using a syringe to protect TPT against hydrolysis by the humidity of the air. After 30 min of stirring, benzene (50 ml) containing *p*-anilinophenol (2.22 g) was added to the flask. The mixture was stirred for 30 h at 70 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature. After filtration, *N*-phenyltetraaniline was extracted with dioxane, silver white microscopic crystals were obtained [0.97 g, 43.9%]. Mp 255—256 °C. The infrared spectrum and elemental analysis of the above mentioned substance were consistent with the presumed structure. Found: C, 81.24; H, 5.92; N, 12.51%. Calcd for $C_{30}H_{26}N_4$: C, 81.42; H, 5.92; N, 12.66%. IR (KBr) ν_{NH} 3360 cm^{-1}; ν_{CH} 1380 cm^{-1}; 1,4-disubstituted benzene rings 810 cm^{-1}; monosubstituted benzene rings 750, 700 cm^{-1}. MS m/z 442 (M^+). Calcd for $C_{30}H_{26}N_4$: 442.

Preparation of *N*-Phenyltetraaniline (2): In a similar way, *N*-phenyltetraaniline was obtained by us of TPT (4.26 g), *p*-anilinoaniline (0.92 g), and *p*-(*p*-anilinoanilino)phenol (1.66 g). The reaction conditions and procedures were almost the same as described above. After extraction with dioxane, silver white microscopic crystals were obtained [0.65 g, 29.4%], Mp 255—256 °C. Found: C, 81.40; H, 5.83; N, 12.62%. Calcd for $C_{30}H_{26}H_4$: C, 81.42; H, 5.92; N, 12.66%. IR (KBr) ν_{NH} 3360 cm^{-1}; ν_{CN} 1380 cm^{-1}; 1,4-disubstituted benzene rings 810 cm^{-1}; monosubstituted benzene rings 750, 700 cm^{-1}. MS m/z 442 (M^+). Calcd for $C_{30}H_{26}N_4$: 442.

Preparation of *N*-Phenylpentaaniline (3): In a similar way, *N*-phenylpentaaniline was obtained by use of TPT (17.0 g) 4,4′-diaminodiphenylamine (1.99 g), and *p*-anilinophenol (3.70 g). The reaction conditions and procedures were almost the same as described above. After extraction with dioxane, silver white microscopic crystals were obtained [1.92 g, 36.0%]. Mp 280—281 °C. Found: C, 81.08; H, 5.75; N, 13.13%. Calcd for $C_{36}H_{31}N_5$; C, 81.02; H, 5.86; N, 13.12%. IR (KBr) ν_{NH} 3360 cm^{-1}; ν_{CN} 1380 cm^{-1}; 1,4-disubstituted benzene rings 810 cm^{-1};monosubstituted benzene rings 750, 700 cm^{-1}, MS m/z 534 (M^+). Calcd for $C_{36}H_{31}N_5$: 534.

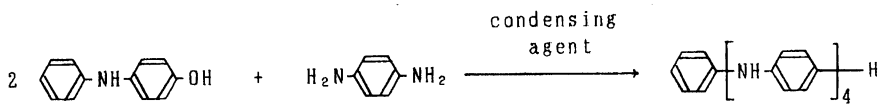
Preparation of *N*-Phenylpentaaniline (4): In a similar way, *N*-phenylpentaaniline was obtained by use of



Scheme 1. Preparation of various titanium alkoxide aryloxides.

Table 1. Preparation of Titanium Alkoxide Aryloxide and Titanium Analyses Data

Titanium alkoxide	Aryl acetate I	Molar Ratio TBT : I	Ti analysis (%) Obsd	Calcd
$Ti(OBu^n)_3(OPh)$	Phenyl Acetate	1 : 1	13.27	13.29
$Ti(OBu^n)_3(OPh)_2$	Phenyl Acetate	1 : 2	12.67	12.59
$Ti(OBu^n)_3(OC_6H_4Me)$	*p*-Tolyl acetate	1 : 1	12.80	12.79
$Ti(OBu^n)_2(OC_6H_4Me)_2$	*p*-Tolyl acetate	1 : 2	11.62	11.73
$Ti(OBu^n)_3(OC_6H_4OMe)$	*p*-Methoxyphenyl acetate	1 : 1	12.28	12.27
$Ti(OBu^n)_2(OC_6H_4OMe)_2$	*p*-Methoxyphenyl acetate	1 : 2	10.88	10.88



II III

Scheme 2. Preparation of *N*-phenyltetraaniline.

TPT (17.0 g), *p*-anilinoaniline (3.68 g), and 4,4′-dihydroxydiphenylamine (2.01 g). The reaction conditions and procedures were almost the same as described above. After extraction with dioxane, silver white microscopic crystals were obtained [1.84 g, 34.5%]. Mp 280—281 °C. Found: C, 81.04; H, 5.97; N, 12.83%. Calcd for $C_{36}H_{31}N_5$: C, 81.02; H, 5.86; N, 13.12%. IR (KBr) ν_{NH} 3360 cm^{-1}; ν_{CN} 1380 cm^{-1}; 1,4-disubstituted benzene rings 810 cm^{-1}; monosubstituted benzene rings 750, 700 cm^{-1}, MS *m/z* 534 (M^+). Calcd for $C_{36}H_{31}N_5$: 534.

Preparation of *N*-*p*-Aminophenyltetraaniline (5): The synthetic method is almost the same as that for preparation of *N*-phenyltetraaniline, *N*-*p*-aminophenyltetraaniline was obtained by the reaction of 4,4′-diaminodiphenylamine (1.99 g) and *p*-(*p*-anilino-anilino)phenol (3.32 g) using TPT (8.53 g) as the condensing agent. After extraction with dioxane, silver white microscopic crystals were obtained [3.05 g, 66.7%]. Mp 253—256 °C. Found: C, 78.75; H, 5.97; N, 15.31%. Calcd for $C_{36}H_{27}N_5$: C, 78.49; H, 5.93; N, 15.11%. IR (KBr) ν_{NH} 3360 cm^{-1}; ν_{CN} 1380 cm^{-1}; 1,4-disubstituted benzene rings 810 cm^{-1}; monosubstituted benzene rings 750, 700 cm^{-1}. MS *m/z* 457 (M^+). Calcd for $C_{36}H_{27}N_5$: 457.

Results and Discussion

Preparation of Various Condensing Agents. The various condensing agents such as titanium alkoxide aryloxides that have phenoxy or substituted phenoxy groups were prepared by the reaction of aryl acetate with titanium alkoxide. The reaction scheme is shown in Scheme 1 and the results are summarized in Table 1. The analytical data agreed with the calcd values.

Preparation of *N*-Phenyltetraaniline. The reaction of *p*-phenylenediamine with *p*-anilinophenol in benzene at 70 °C using TBT gave *N*-phenyltetraaniline as silver white microscopic crystals (41.9% yield). Especially *N*-phenyltetraaniline were prepared in excellent yield by the reaction of II and III using titanium alkoxide aryloxides that have phenoxy or substituted phenoxy groups.

The reaction scheme is shown in Scheme 2. These results are summarized in Table 2. Effects of substituents of aromatic rings in titanium alkoxide on the yields of *N*-phenyltetraaniline are shown in Fig. 1.

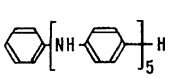
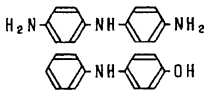
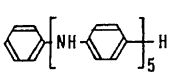
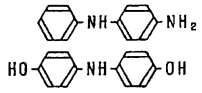
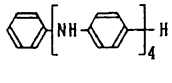
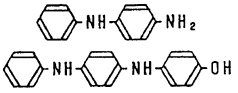
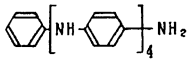
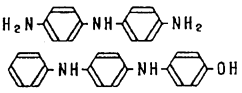
It should be noted that titanium alkoxide aryl-

Table 2. Yields, Melting Points, and Elemental Analyses Data of *N*-Phenyltetraaniline[a)]

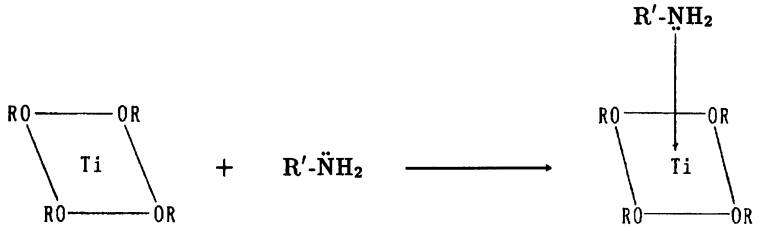
Condensing agent	Yield	Mp	Found (%)		
	%	θ/°C	H	C	N
$Ti(OPr^i)_4$	43.9	255—256	5.92	81.24	12.51
$Ti(OBu^n)_4$	70.5	255—256	5.92	81.23	12.51
$Ti(OBu^n)_3(OPh)$	87.5	255—256	5.93	81.20	12.37
$Ti(OBu^n)_2(OPh)_2$	75.6	255—256	5.86	81.21	12.41
$Ti(OBu^n)_3(OC_6H_4Me)$	91.2	255—256	5.88	81.32	12.46
$Ti(OBu^n)_2(OC_6H_4Me)_2$	75.9	253—256	5.88	81.59	12.51
$Ti(OBu^n)_3(OC_6H_4OMe)$	64.3	255—256	5.87	81.59	12.48
$Ti(OBu^n)_2(OC_6H_4OMe)_2$	47.4	254—255	5.86	81.69	12.49

a) Reaction time 30 h. Calcd for $C_{30}H_{26}N_4$: H, 5.92; C, 81.42; N, 12.66%.

Table 3. Preparation of Various Oligoaniline Derivatives: Starting Materials, Yield, and Elemental Analyses

Compound	Amines / Phenols	Yield %	Elemental analysis (%) Found (Calcd) H	C	N
		36.0	5.75 (5.86)	81.08 (81.02)	13.13 (13.12)
		34.5	5.97	81.04	12.83
		29.4	5.83 (5.92)	81.40 (81.42)	12.62 (12.66)
		66.7	5.97 (5.93)	78.75 (78.49)	15.31 (15.11)

Condensing agent: TPT.



Scheme 3. Formation of complex with amine as intermediate.

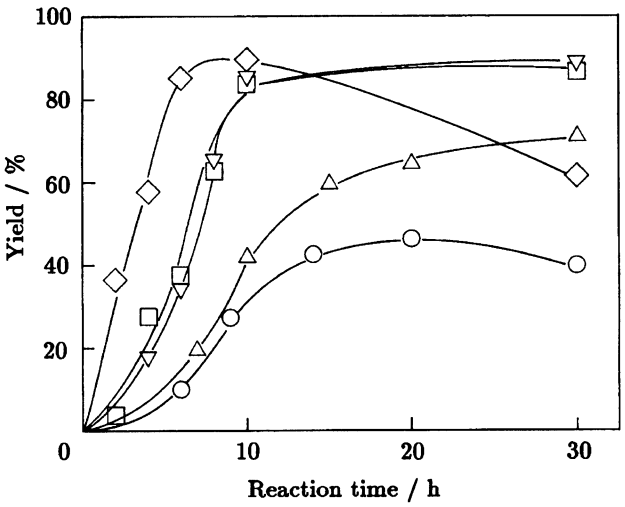


Fig. 1. Correlation between yield and reaction time of preparation of *N*-phenyltetraaniline. ○; Ti(OPr^i)$_4$, △; Ti(OBu^n)$_4$, ▽; Ti(OBu^n)$_3$(OPh), □; Ti(OBu^n)$_3$(OC$_6$H$_4$Me), ◇; Ti(OBu^n)$_3$(OC$_6$H$_4$OMe)

oxides, particularly, titanium tributoxide *p*-methoxyphenoxides, have higher dehydration condensation properties than titanium alkoxides. Judging from this result, the yield of the preparation of *N*-phenyltetraaniline using such titanium alkoxides and titanium alkoxide aryloxides increased in the order: Ti(OPr^i)$_4$ < Ti(OBu^n)$_4$ < Ti(OBu^n)$_3$(OC$_6$H$_5$)≈ Ti(OBu^n)$_3$(OC$_6$H$_4$Me) < Ti(OBu^n)$_3$(OC$_6$H$_4$OMe).

Titanium diphenoxides as condensing agents, however, were inferior to titanium monophenoxides in the preparation of *N*-phenyltetraaniline for dehydration condensation activity.

Preparation of Linear Oligoaniline Derivatives. Preparation of various oligoaniline derivatives such as *N*-phenyltetraaniline, *N*-phenylpentaaniline, *N*-*p*-aminophenyltetraaniline using various starting materials were investigated. These results are listed in Table 3.

In the course of our study the role of titanium alkoxide aryloxide for preparation of linear oligoaniline derivatives were thought to be as follows Scheme 3.

Titanium alkoxide aryloxides formed stable com-

plexes with amines[8] in the reaction mixture, then, dehydration condensation occurred to the amine complex and phenols to give linear oligoaniline derivatives.

To separate the amine complexes from the reaction mixture as solids, further studies are now under investigation.

In conclusion, this method considered to be an efficient route to prepare oligoaniline derivatives in good yields. Especially, using titanium alkoxide aryloxide, *N*-phenyltetraaniline was obtained in high yield. However, the mechanism of the reaction and effects of the substituent on the phenyl groups in titanates cannot be defined precisely. To understand the effects of the groups in titanates, further studies are required concerning the influence of substituted groups in titanates.

Finally, we are grateful to Dr. Teiji Tsuruta for helpful comments and useful suggestions, and we would like to express our thanks to Mr. Yoshiyuki Miki for elemental analyses and IR spectra recordings.

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