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Preparation of 3-Substituted Quinolines. I. Alkylation of Malonaldehyde Dianil Derivatives

REIKO TODORIKI, MACHIKO ONO, and SHINZO TAMURA*

School of Pharmaceutical Science, Toho University, 2-2-1, Miyama, Funabashi 274, Japan

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2-Substituted 1-arylamino-3-arylimino-1-propenes (III) were prepared by the reaction of *N*-lithio derivatives of 1-arylamino-3-arylimino-1-propenes (malonaldehyde dianil derivatives) (II) and substituted benzyl bromides. 2-Allyl and 2-(2,4-dinitrophenyl) derivatives of II were prepared by the same method. However, the alkylation failed with less reactive alkyl halides such as ethyl iodide as alkylating agents. Hydrolysis of III afforded α-substituted β-(arylamino)acroleins (IV), which afforded 3-substituted quinolines (V) on heating with aluminium chloride.

Keywords——2-alkyl-1-arylamino-3-arylimino-1-propene; α-alkyl-β-(arylamino)acrolein; 3-alkylquinoline; alkylation; hydrolysis; cyclodehydration

In previous papers we reported a synthetic method for quinolines by cyclodehydration of β-(arylamino)acroleins (I)[1] and preparation of β-(arylamino)acroleins by hydrolysis of 1-arylamino-3-arylimino-1-propenes (malonaldehyde dianil derivatives) (II).[2] In this paper we wish to report the preparation of 2-substituted 1-arylamino-3-arylimino-1-propenes (III) by the alkylation of II, hydrolysis of III to form α-substituted β-(arylamino)acroleins (IV), and cyclodehydration of IV to form 3-substituted quinolines (V) (Chart 1).

N^1,N^2-Diarylamidines are known to be alkylated by alkyl halides only at higher temperature than in the alkylation of primary amines. Pyman[3] had obtained N^1-methyl-N^2-(*p*-nitrophenyl)-N^1-phenylbenzamidine and N^1-methyl-N^1-(*p*-nitrophenyl)-N^2-phenylbenzamidine from N^1-(*p*-nitrophenyl)-N^2-phenylbenzamidine on heating with excess methyl iodide with some recovery of the starting material, while *N*-ethyl-*m*-toluidine is formed from *m*-toluidine and ethyl bromide merely on standing at room temperature.[4]

Malonaldehyde dianils, which are vinylogs of N^1,N^2-diarylamidines, resist alkylation with alkyl halides to a larger extent than N^1,N^2-diarylamidine. When a solution of 1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (malonaldehyde dianil of *p*-toluidine) (IIa) and benzyl bromide in tetrahydrofuran was refluxed for 90 min, small amounts of 1-(*N*-benzyl-*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (VI) and *N*-benzyl-β-(*p*-toluidino)acrolein (VIIa) were detected in the reaction mixture, while a larger amount of IIa was recovered unchanged (Chart 2).

Fisher prepared the *N*-lithio derivative (VIII) of 1-phenylamino-3-phenylimino-1-propene (IIb) by treating IIb with an equimolar amount of *n*-buthyllithium,[5] and found that the 2-position of VIII has a high electron density on the basis of the observation that the signal of the 2-position of VIII appeared at higher applied field as compared with that of IIb in the ^{1}H nuclear magnetic resonance (^{1}H-NMR) spectrum.[6] This fact suggests that *N*-lithio derivatives of malonaldehyde dianils might undergo alkylation at 2-position with alkyl halides (Chart 3).

2-Benzyl-1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (IIIa) was obtained when the *N*-lithio derivative of 1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (IIa) was allowed to react with benzyl bromide at room temperature under a nitrogen

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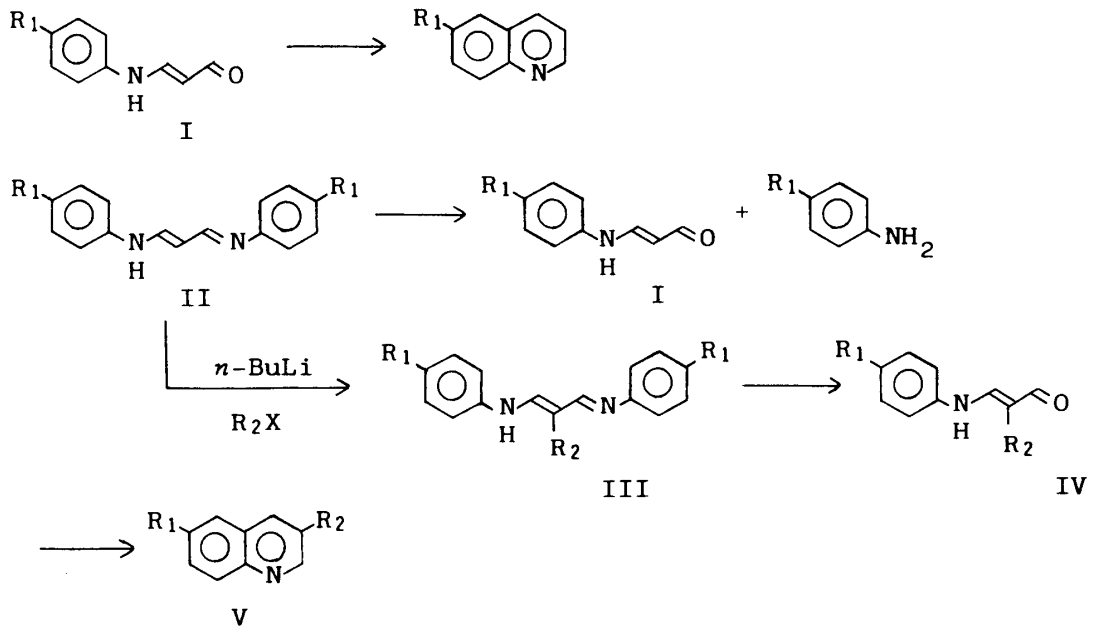
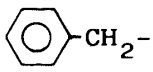
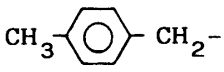
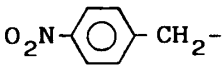
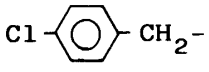


	Ia	Ib	Ic	IIa	IIb
R1:	CH_3-	H-	Cl-	CH_3-	H-

	IIIa	IIIb	IIIc	IIId
	IVa	IVb	IVc	IVd
	Va	Vb		Vd
R1:	CH_3-	CH_3-	CH_3-	CH_3-
R2:				

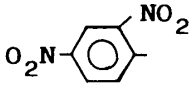
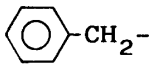
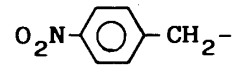
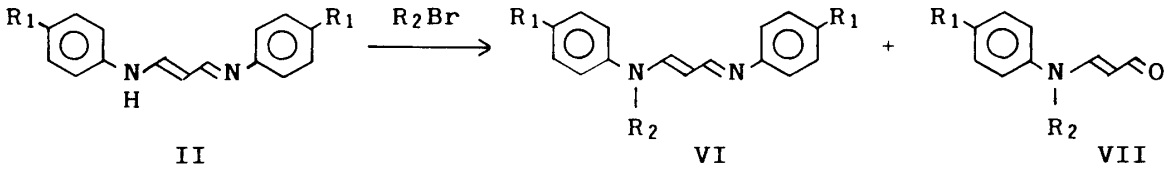
	IIIe	IIIf	IIIg	IIIh
	IVe		IVg	IVh
			Vg	Vh
R1:	CH_3-	CH_3-	H-	H-
R2:	CH_2=CH-CH_2-			

Chart 1



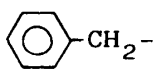
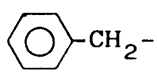
	VI	VIIa
R1:	CH_3-	CH_3-
R2:		

Chart 2

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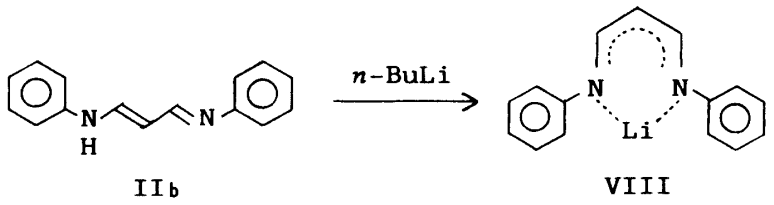

IIb VIII

Chart 3

atmosphere. The results of elemental analysis were consistent with the values required for the molecular formula $C_{24}H_{24}N_2$. The ^{1}H-NMR spectrum (chloroform-*d*) showed signals at δ2.25 (6H, methyl groups, singlet), 3.55 (2H, methylene, singlet) and 7.48 (2H, 1- and 3-positions, singlet). 2-(*p*-Methylbenzyl)-1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (IIIb), 1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-2-(*p*-nitrobenzyl)-1-propene (IIIc) and 2-(*p*-chlorobenzyl)-1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (IIId) were prepared by the same method (Chart 1). In the reaction of IIa and *p*-chlorobenzyl bromide, two by-products (IX and X) were obtained. The results of elemental analysis of IX and of X were both consistent with the values required for the molecular formula of $C_{31}H_{28}Cl_2N_2$. The structures of IX and X were elucidated by ^{1}H-NMR spectroscopy to be 2,2-bis(*p*-chlorobenzyl)-1,3-bis(*p*-methylphenylimino)propene and 2,*N*-bis(*p*-chlorobenzyl)-1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene, respectively (Chart 4). The ^{1}H-NMR spectrum (chloroform-*d*) of IX showed signals at δ2.30 (6H, methyl groups, singlet), 3.28 (4H, methylene groups, singlet) and 7.88 (2H, 1- and 3-positions, singlet), and that of X showed signals at δ2.18 (3H, methyl, singlet), 2.28 (3H, methyl, singlet), 3.26 (2H, methylene at 2-position, singlet), 4.43 (2H, methylene at nitrogen atom, singlet) and 7.90 (1H, 3-position, singlet). The signal of the 1-position of X could not be distinguished because the signal overlapped with those of the aryl groups. Compound IX as well as X could not be detected in the reaction mixture when the *N*-lithio derivative of IIId was allowed to react with an equimolar amount of *p*-chlorobenzyl bromide in tetrahydrofuran solution at room temperature for 1 d under a nitrogen atmosphere. The course of the formation of IX and X, therefore, is not yet clear.

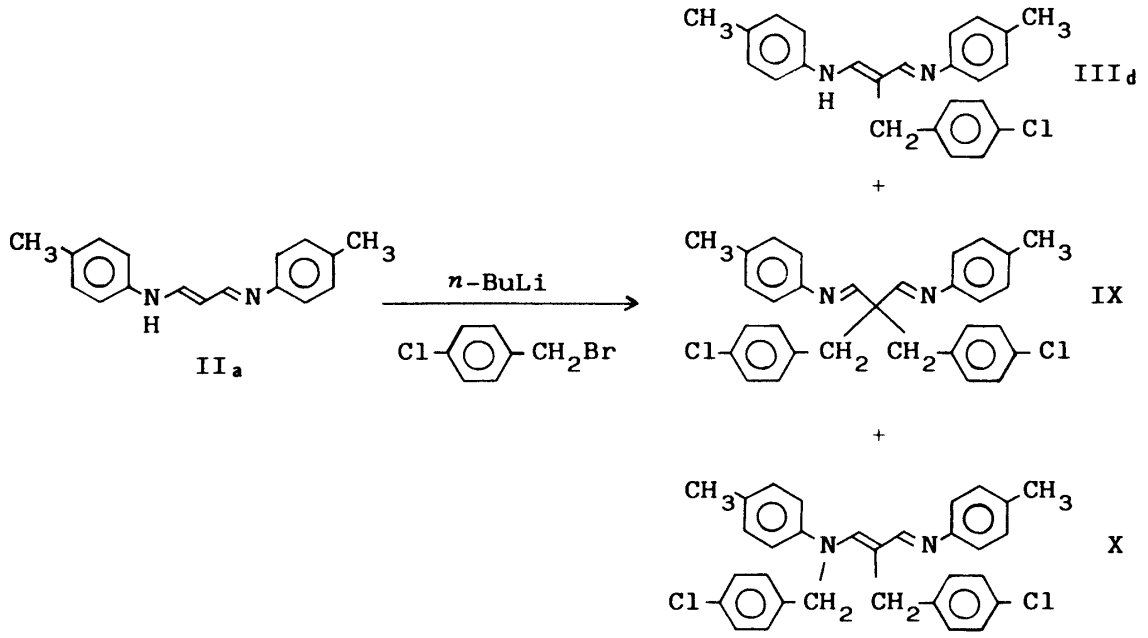

Chart 4

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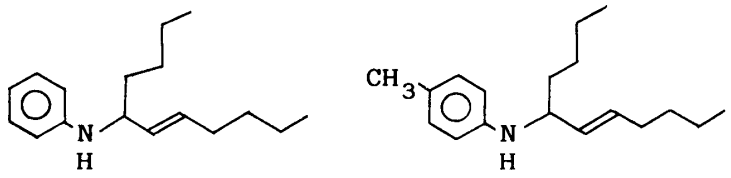
The 2-alkyl derivative of IIa could not be detected in the reaction mixture of the *N*-lithio derivative of IIa and ethyl iodide, phenethyl bromide or isopropyl bromide. The isolated products were only small amounts of *N*-ethyl-*p*-toluidine and *p*-toluidine besides recovered starting material (IIa) when a tetrahydrofuran solution of the *N*-lithio derivative of IIa and ethyl iodide was refluxed for 2 h under a nitrogen atmosphere. The alkylation at the 2-position of the *N*-lithio derivative of II occurs only on employing highly reactive alkyl halides. 2-Allyl-1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (IIIe) and 2-(2,4-dinitrophenyl)-1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (IIIf) were obtained by the reaction of the *N*-lithio derivative of IIa and the corresponding halides. A liquid substance was obtained as a by-product in the reaction of IIa and 2,4-dinitrochlorobenzene.

Fisher obtained 7-anilino-5-undecene (XI) as a liquid by the reaction of IIb and excess *n*-butyllithium.[5] By the application of this method to IIa, 7-(*p*-toluidino)-5-undecene (XII) was obtained (Chart 5). The ^{1}H-NMR spectrum of XII showed an identical pattern to that of the liquid substance isolated as a by-product of the preparation of IIIf (Fig. 1).



XI XII

Chart 5

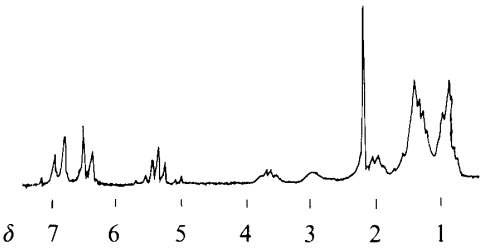
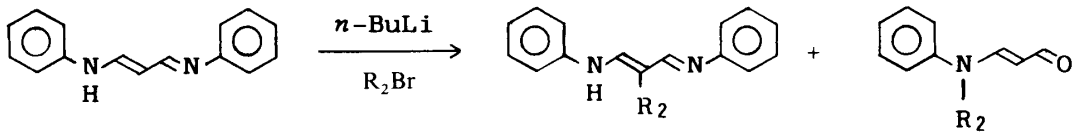


Fig. 1. ^{1}H-NMR Spectrum ($CDCl_3$) of XII



IIb III VII

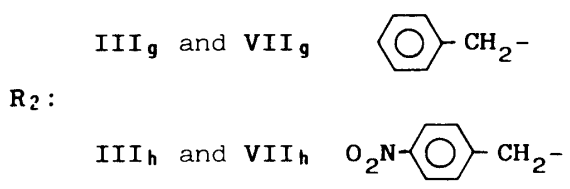


Chart 6

N-Alkylation proceeded in parallel to the alkylation at the 2-position in the reaction of the *N*-lithio derivative of IIb with benzyl bromide. 2-Benzyl-1-phenylamino-3-phenylimino-1-propene (IIIg) and a small amount of *N*-benzyl-*β*-anilinoacrolein (VIIg) were obtaind. Similar

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results were obtained in the reaction of IIb and *p*-nitrobenzyl bromide. The ^{1}H-NMR spectra of the crude products of the above two reactions suggested that the products contained a small amount of XI (Chart 6).

Hydrolysis of III was achieved in a similar manner to that used for the preparation of β-(arylamino)acrolein from II.[2] Compound IV and arylamine were formed (except in the case of IIIf) when an aqueous ethanolic solution of III was refluxed in the presence of 0.1 eq amount of acetic acid and 0.9 eq amount of sodium acetate. Compound IIIf was recovered unchanged after the above treatment (Chart 1).

We had previously employed aluminium chloride as a catalyst for cyclodehydration of I without any solvent and in tetrachloroethane or nitrobenzene solution.[1] The results of the reaction in nitrobenzene solution were rather unsatisfactory. In the cyclodehydration of I by aluminium chloride without solvent, a higher temperature than the melting point of I was necessary to initiate the reaction because both substances are solid. In the previous work,[1] cyclodehydrations of β-(*p*-toluidino)acrolein (Ia), β-anilinoacrolein (Ib) and β-(*p*-chloroanilino)acrolein (Ic) with aluminium chloride were carried out by heating at 120 °C.

With aluminium bromide as a cyclodehydration agent (it has a much lower melting point than aluminium chloride), the reaction mixture became homogeneous on heating at 80 °C in the cyclodehydration of Ia—c. The corresponding quinolines were obtained in good yields on heating a mixture of Ia—c and aluminium bromide (molar ratio 1 : 3) at 80 °C for 30 min. No quinolines were detected in the reaction mixture, however, when Ia—c and aluminium bromide were heated at 120 °C in tetrachloroethane solution. With nitrobenzene as a solvent formation of small amount of quinolines was observed under similar conditions. A small amount of *p*-bromoaniline was also detected in the reaction mixture. Gilman *et al.*[7] reported the formation of *o*-chloro- and *p*-chloroaniline on standing of a nitrobenzene solution of isobutyl bromide and aluminium chloride at room temperature for 30 d. Small amounts of *p*-bromoaniline and 2,4-dibromoaniline were formed when a solution of aluminium bromide in nitrobenzene was heated at 120—140 °C for 6 h. Nitrobenzene is, therefore, not a suitable solvent for the cyclodehydration of I in the presence of aluminium halides.

The cyclodehydration of IVa was examined on heating with aluminium bromide. However, the expected 3-benzyl-6-methylquinoline (Va) could not be detected in a reaction mixture in which a mixture of IVa and aluminium bromide (molar ratio 1 : 3) was heated at 120—140 °C for 5 h, though 6-methylquinoline was isolated in 37% yield. Similar results were obtained by treating IVb and IVd under the same conditions.

3-Benzylquinoline (Vg) was recovered in 20% yield on heating with aluminium bromide at 120—140 °C for 5 h. No quinoline could be detected in the reaction mixture. The above debenzylation occurred, therefore, not in the reaction of V and aluminium bromide, but in the reaction of IV and aluminium bromide. 6-Methylquinoline was recovered in nearly quantitative yield on heating with aluminium bromide or aluminium chloride at 120—140 °C for 5 h, in contrast to the case of Vg.

The cyclodehydration of IV was examined on heating with aluminium chloride. The starting materials (62%) was recovered on heating a mixture of IVg and aluminium chloride at 120 °C for 5 h. No 3-benzylquinoline (Vg) was detected in the reaction mixture. For the initiation of the cyclodehydration of IV, it was necessary to heat a mixture of IV and aluminium chloride at a higher temperature than 170 °C, except in the case of α-(*p*-nitrobenzyl)-β-anilinoacrolein (IVh). On heating a mixture of IV and aluminium chloride (molar ratio 1 : 3) at a higher temperature than 170 °C, the corresponding quinolines were obtained in 27—33% yields. In the cyclodehydration of IVb, a small amount of 6-methylquinoline was obtained as a by-product, suggesting that the debenzylation of IVb occurred to some extent even with aluminium chloride as a cyclodehydrating agent. 3-Allyl-6-methylquinoline could not be detected in the reaction mixture when a mixture of IVe and

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aluminium chloride was heated at 190—200 °C or at 140—160 °C for 5 h. 3-(*p*-Nitrobenzyl)quinoline (Vh) was obtained in rather unsatisfactory yield (7%) when a mixture of IVh and aluminium chloride was heated at 140—160 °C for 5 h. No quinoline derivative was detected when the above mixture was heated at 190—200 °C. This cyclodehydrating method is, therefore, not suitable for β-(arylamino)acrolein derivatives containing a nitro group.

Experimental

All melting points are uncorrected. The ^{1}H-NMR spectra were recorded on a JNM-PMX 60 NMR spectrometer with tetramethylsilane as an internal standard. The following abbreviations are used: singlet (s), doublet (d), double doublet (dd) and multiplet (m).

The samples of *p*-toluidine, 2,4-dinitrophenol, acetanilide, *N*-acetyl-*p*-toluidine, *N*-acetyl-*p*-chloroaniline, *p*-bromoaniline and 2,4-dibromoaniline described in this section were identical with corresponding authentic samples on the basis of mixed melting point measurement and comparison of infrared (IR) spectra. The samples of quinoline, 6-methylquinoline and 6-chloroquinoline described in this section were converted into their picrates, which were identified by comparison with corresponding authentic samples (mixed melting point measurement).

Reaction of IIa and Benzyl Bromide——A solution of 2.50 g (0.01 mol) of IIa and 0.85 g (0.005 mol) of benzyl bromide in 20 ml of anhydrous tetrahydrofuran (THF) was refluxed for 90 min. The deposited precipitate was filtered with suction, and treated with 7% $NaHCO_3$ to give 1.02 g (41%) of the starting material (IIa). The filtrate was concentrated under reduced pressure, and the residue was dissolved in $CHCl_3$. The $CHCl_3$ solution was washed with 7% $NaHCO_3$, dried over K_2CO_3, and concentrated under reduced pressure. A small amount of petroleum benzin was added to the residue, and the deposited precipitate was filtered with suction, and recrystallized from petroleum benzin to give 0.38 g (11%) of VI. mp 119 °C. *Anal.* Calcd for $C_{24}H_{24}N_2$: C, 84.67; H, 7.11; N, 8.23. Found: C, 84.19; H, 7.20; N, 8.06. ^{1}H-NMR ($CDCl_3$) δ: 2.28 (6H, $2CH_3$, s), 4.83 (2H, CH_2, s), 5.62 (1H, 2-position, dd, J=9, 13 Hz), 7.50 (1H, 1-position, d, J=13 Hz) and 7.92 (1H, 3-position, d, J=9 Hz). The filtrate was subjected to column chromatography (Al_2O_3) with benzene and benzene–AcOEt (5 : 1) to give a small amount of *p*-toluidine and crude VIIa, and the latter was distilled under reduced pressure (0.2 Torr, bath temperature 190 °C) to give 0.16 g (6%) of pure VIIa. An oil. *Anal.* Calcd for $C_{17}H_{17}NO \cdot 1/4H_2O$: C, 79.81; H, 6.90; N, 5.48. Found: C, 80.32; H, 7.03; N, 6.02. ^{1}H-NMR ($CDCl_3$) δ: 2.27 (3H, CH_3, s) 4.75 (2H, CH_2, s), 5.23 (1H, α-position, dd, J=8, 13 Hz), 7.45 (1H, β-position, d, J=13 Hz) and 9.08 (1H, CHO, d, J=8 Hz).

Preparation of 2-Benzyl-1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (IIIa)——A 15% *n*-hexane solution of *n*-BuLi (8.2 ml, 0.019 mol) was added to a solution of 4.00 g (0.016 mol) of IIa in 50 ml of anhydrous THF under N_2. A solution of 2.73 g (0.016 mol) of benzyl bromide in 10 ml of anhydrous THF was added to the mixture under water-cooling, and the whole was immediately concentrated under reduced pressure. The residue was dissolved in $CHCl_3$, and the $CHCl_3$ solution was washed with 7% $NaHCO_3$, dried over K_2CO_3, and concentrated under reduced pressure. A small amount of EtOH was added to the residue, and the deposited precipitate was collected and recrystallized from EtOH to give 1.89 g (35%) of IIIa. mp 111 °C. *Anal.* Calcd for: $C_{24}H_{24}N_2$: C, 84.67; H, 7.11; N, 8.23. Found: C, 84.35; H, 7.18; N, 8.17.

Preparation of 2-(*p*-Methylbenzyl)-1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (IIIb)——A 15% *n*-hexane solution of *n*-BuLi (6.2 ml, 0.0145 mol) was added to a solution of 3.00 g (0.012 mol) of IIa in 50 ml of anhydrous THF under N_2. A solution of 2.22 g (0.012 mol) of *p*-methylbenzyl bromide in 10 ml of anhydrous THF was added to the mixture under water-cooling. The whole was immediately concentrated under reduced pressure. The residue was dissolved in $CHCl_3$, and the $CHCl_3$ solution was washed with 7% $NaHCO_3$, dried over K_2CO_3, and concentrated under reduced pressure. The residue was dissolved in THF, and the solution was added to a stirred mixture of 150 ml of 0.01 N HCl and 150 ml of ether. The deposited precipitate (hydrochloride of IIIb, 2.00 g) was collected. mp 218 °C (dec.). *Anal.* Calcd for $C_{25}H_{26}N_2 \cdot 2HCl \cdot H_2O$: C, 67.41; H, 6.79; N, 6.29. Found: C, 67.44; H, 6.26; N, 6.13. The hydrochloride was treated with 7% $NaHCO_3$ to give IIIb. An oil. ^{1}H-NMR ($CDCl_3$) δ: 2.23 (9H, $3CH_3$, s), 3.50 (2H, CH_2, s) and 7.47 (2H, 1- and 3-positions, s).

Preparation of 1-(*p*-Methylphenylamino)-3-(*p*-methylphenylimino)-2-(*p*-nitrobenzyl)-1-propene (IIIc)——A 15% *n*-hexane solution of *n*-BuLi (10.6 ml, 0.025 mol) was added to a solution of 5.00 g (0.02 mol) of IIa in 50 ml of anhydrous THF under N_2. A solution of 4.32 g (0.02 mol) of *p*-nitrobenzyl bromide in 20 ml of anhydrous THF was added to the mixture under water-cooling. The whole was immediately concentrated under reduced pressure, and the residue was dissolved in $CHCl_3$. The $CHCl_3$ solution was washed with 7% $NaHCO_3$, dried over K_2CO_3, and concentrated under reduced pressure. A small amount of EtOH was added to the residue, and the deposited precipitate was collected and recrystallized from EtOH to give 4.03 g (52%) of IIIc. mp 124 °C. *Anal.* Calcd for $C_{24}H_{23}N_3O_2 \cdot 1/4H_2O$: C, 73.92; H, 6.07; N, 10.78. Found: C, 73.90; H, 6.14; N, 10.70. ^{1}H-NMR ($CDCl_3$) δ: 2.27 (6H, $2CH_3$, s), 3.67 (2H, CH_2, s) and 7.48 (2H, 1- and 3-positions, s).

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Preparation of 2-(*p*-Chlorobenzyl)-1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (IIId)——A 15% *n*-hexane solution of *n*-BuLi (10.6 ml, 0.025 mol) was added to a solution of 5.00 g (0.02 mol) of IIa in 50 ml of anhydrous THF under N_2. A solution of 4.10 g (0.02 mol) of *p*-chlorobenzyl bromide in 10 ml of anhydrous THF was added to the mixture under water-cooling. The whole was immediately concentrated under reduced pressure. The residue was dissolved in $CHCl_3$, and the $CHCl_3$ solution was washed with 7% $NaHCO_3$, dried over K_2CO_3, and concentrated under reduced pressure. A small amount of EtOH was added to the residue. The deposited precipitate was filtered with suction to give 0.76 g of IX. mp 153 °C. *Anal.* Calcd for $C_{31}H_{28}Cl_2N_2$: C, 74.53; H, 5.65; N, 5.61. Found: C, 74.44; H, 5.74; N, 5.45. The filtrate was added to a stirred mixture of 300 ml of 0.2 N HCl and 300 ml of ether. The deposited precipitate was collected to give 4.25 g of hydrochloride of IIId. mp 171 °C (dec.). *Anal.* Calcd for $C_{24}H_{23}ClN_2 \cdot HCl \cdot 3/2H_2O$: C, 65.75; H, 6.21; N, 6.39. Found: C, 65.57; H, 5.83; N, 6.25. The hydrochloride was treated with 7% $NaHCO_3$ to give IIId. An oil. ^{1}H-NMR ($CDCl_3$) δ: 2.23 (6H, $2CH_3$, s) 3.53 (2H, CH_2, s) and 7.42 (2H, 1- and 3-positions, s).

In a repeated experiment, 0.62 g of X was obtained as an EtOH-insoluble component. mp 105 °C. *Anal.* Calcd for $C_{31}H_{28}Cl_2N_2 \cdot 1/2H_2O$: C, 73.32; H, 5.75; N, 5.51. Found: C, 73.69; H, 5.59; N, 5.07.

Preparation of 2-Allyl-1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (IIIe)——A 15% *n*-hexane solution of *n*-BuLi (9.0 ml, 0.021 mol) was added to a solution of 5.00 g (0.02 mol) of IIa in 30 ml of anhydrous THF under N_2. A solution of 2.40 g (0.02 mol) of allyl bromide in 7 ml of anhydrous THF was added to the mixture under water-cooling. The whole was refluxed for 18 h, and concentrated under reduced pressure. The residue was dissolved in $CHCl_3$, and the $CHCl_3$ solution was washed with 7% $NaHCO_3$, dried over K_2CO_3, and concentrated under reduced pressure. The residue was dissolved in THF, and the solution was added to a stirred mixture of 400 ml of 0.1 N HCl and 300 ml of ether. The deposited precipitate was collected to give 2.23 g of hydrochloride of IIIe. mp 235 °C (dec.). *Anal.* Calcd for $C_{20}H_{22}N_2 \cdot HCl$: C, 73.49; H, 7.09; N, 8.57. Found: C, 73.63; H, 7.11; N, 8.35. The hydrochloride was treated with 7% $NaHCO_3$ to give IIIe. An oil. ^{1}H-NMR ($CDCl_3$) δ: 2.20 (6H, $2CH_3$, s), 3.00 (2H, $-CH_2-$, m), 4.97 and 5.02 (each 1H, $=CH_2$, m), 5.87 (1H, $-CH=$, m) and 7.40 (2H, 1- and 3-positions, s).

Preparation of 2-(2,4-Dinitrophenyl)-1-(*p*-methylphenylamino)-3-(*p*-methylphenylimino)-1-propene (IIIf)——A 15% *n*-hexane solution of *n*-BuLi (9 ml, 0.021 mol) was added to a solution of 5.00 g (0.02 mol) of IIa in 30 ml of anhydrous THF under N_2. A solution of 4.20 g (0.02 mol) of 2,4-dinitrochlorobenzene in 5 ml of anhydrous THF was added to the mixture under water-cooling. The whole was immediately concentrated under reduced pressure, and the residue was dissolved in $CHCl_3$. The $CHCl_3$ solution was extracted with 7% $NaHCO_3$. The $NaHCO_3$ layer was treated as usual to give a small amount of 2,4-dinitrophenol. The $CHCl_3$ layer was dried over K_2CO_3, and concentrated under reduced pressure. A small amount of $CHCl_3$ was added to the residue, and the deposited precipitate was filtered with suction to give the hydrochloride of IIa. The hydrochloride was treated with 7% $NaHCO_3$ to give 0.64 g (13%) of IIa. The filtrate was concentrated under reduced pressure. A small amount of ether was added to the residue, and the deposited precipitate was filtered with suction, and recrystallized from benzene to give 3.38 g (41%) of IIIf. mp 191 °C (dec.). *Anal.* Calcd for $C_{23}H_{20}N_4O_4$: C, 66.34; H, 4.84; N, 13.45. Found: C, 66.63; H, 4.76; N, 13.47. ^{1}H-NMR ($CDCl_3$) δ: 2.32 (6H, $2CH_3$, s) and 7.72 (2H, 1- and 3-positions, s). The filtrate was concentrated under reduced pressure, and the residue was subjected to column chromatography (Al_2O_3) with petroleum benzin, benzene and AcOEt to give small amounts of XII and *N*-(2,4-dinitrophenyl)-β-(*p*-toluidino)acrolein (VIIf); the latter was recrystallized from petroleum benzin. mp 133 °C. *Anal.* Calcd for $C_{16}H_{13}N_3O_5$: C, 58.72; H, 4.00; N, 12.84. Found: C, 58.82; H, 3.88; N, 12.53. ^{1}H-NMR ($CDCl_3$) δ: 2.33 (3H, CH_3, s), 5.35 (1H, α-position, dd, $J=8$, 13 Hz), 7.35 (1H, β-position, d, $J=13$ Hz) and 9.27 (1H, CHO, d, $J=8$ Hz).

Preparation of 2-Benzyl-1-phenylamino-3-phenylimino-1-propene (IIIg)——A 15% *n*-hexane solution of *n*-BuLi (9.0 ml, 0.021 mol) was added to a solution of 4.50 g (0.02 mol) of IIb in 40 ml of anhydrous THF under N_2. A solution of 3.40 g (0.02 mol) of benzyl bromide in 10 ml of anhydrous THF was added to the mixture under water-cooling. The whole was immediately concentrated under reduced pressure. The residue was dissolved in $CHCl_3$. The $CHCl_3$ solution was washed with 7% $NaHCO_3$, dried over K_2CO_3, and concentrated under reduced pressure. A small amount of EtOH was added to the residue. The deposited precipitate was filtered with suction, and recrystallized from petroleum benzin to give 1.06 g (17%) of IIIg. mp 87 °C. *Anal.* Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.48; H, 6.54; N, 8.70. ^{1}H-NMR ($CDCl_3$) δ: 3.65 (2H, CH_2, s) and 7.55 (2H, 1- and 3-positions, s). The filtrate was added to a stirred mixture of 500 ml of 0.04 N HCl and 300 ml of ether. The ether layer was dried over K_2CO_3, and concentrated under reduced pressure. The residue was subjected to column chromatography (Al_2O_3) with benzene–AcOEt to give crude *N*-benzyl-β-anilinoacrolein (VIIg), which was recrystallized from petroleum benzin to give 0.15 g (3%) of pure VIIg. mp 112 °C. *Anal.* Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.64; H, 6.33; N, 5.92. ^{1}H-NMR ($CDCl_3$) δ: 4.83 (2H, CH_2, s), 5.35 (1H, α-position, dd, $J=8$, 13 Hz), 7.53 (1H, β-position, d, $J=13$ Hz) and 9.12 (1H, CHO, d, $J=8$ Hz).

Preparation of 2-(*p*-Nitrobenzyl)-1-phenylamino-3-phenylimino-1-propene (IIIh)——A 15% *n*-hexane solution of *n*-BuLi (22 ml, 0.051 mol) was added to a solution of 10.0 g (0.045 mol) of IIb in 60 ml of anhydrous THF under N_2. A solution of 9.72 g (0.045 mol) of *p*-nitrobenzyl bromide in 20 ml of anhydrous THF was added to the mixture under water-cooling. The whole was immediately concentrated under reduced pressure. The residue was dissolved in $CHCl_3$, and the $CHCl_3$ solution was washed with 7% $NaHCO_3$, dried over K_2CO_3, and concentrated under reduced

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pressure. A small amount of $CHCl_3$ was added to the residue, and the deposited precipitate was filtered with suction, and recrystallized from benzene to give 4.82 g (30%) of IIIh. mp 185 °C. *Anal.* Calcd for $C_{22}H_{24}N_3O_2$: C, 73.93; H, 5.36; N, 11.76. Found: C, 73.68; H, 5.22; N, 11.32. ^{1}H-NMR ($CDCl_3$) δ: 3.75 (2H, CH_2, s) and 7.53 (2H, 1- and 3-positions, s). The filtrate was concentrated under reduced pressure. The residue was subjected to column chromatography (Al_2O_3) with AcOEt to give crude *N*-(*p*-nitrobenzyl)-β-anilinoacrolein (VIIh), which was recrystallized from benzene to give 0.94 g (7%) of pure VIIh. mp 146 °C. *Anal.* Calcd for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.92. Found: C, 68.39; H, 5.11; N, 9.57. ^{1}H-NMR ($CDCl_3$) δ: 4.97 (2H, CH_2, s), 5.27 (1H, α-position, dd, J=8, 13 Hz), 7.58 (1H, β-position, d, J=13 Hz) and 9.22 (1H, CHO, d, J=8 Hz).

Reaction of IIa with Excess *n*-BuLi——A 15% *n*-hexane solution of *n*-BuLi (4.5 ml, 0.01 mol) was added under water-cooling to a solution of 1.25 g (0.005 mol) of IIa in 15 ml of anhydrous THF under N_2. The whole was refluxed for 90 min, then allowed to stand overnight at room temperature. The whole was concentrated under reduced pressure, and the residue was dissolved in $CHCl_3$. The $CHCl_3$ solution was washed with 7% $NaHCO_3$, dried over K_2CO_3, and concentrated under reduced pressure. A small amount of EtOH was added to the residue, and the deposited precipitate was filtered with suction to give 0.50 g (40%) of IIa. The filtrate was concentrated under reduced pressure, and the residue was subjected to column chromatography (Al_2O_3) with petroleum benzin and benzene to give small amounts of crude XII and *p*-toluidine. EtOH–HCl was added to the crude XII, and the whole was concentrated under reduced pressure. The residue was distilled under reduced pressure (0.2 Torr, bath temperature 150 °C) to give 60 mg of the hydrochloride of XII. mp 88 °C. *Anal.* Calcd for $C_{18}H_{29}N \cdot HCl \cdot 1/4H_2O$: C, 71.97; H, 10.23; N, 4.66. Found: C, 72.04; H, 10.43; N, 4.41.

Hydrolysis of III——An aqueous solution of 0.1 eq of AcOH and 0.9 eq of AcONa was added to an ethanolic solution of III. The mixture was refluxed, then 7% $NaHCO_3$ was added. The whole was concentrated under reduced pressure. The deposited precipitate was collected, and recrystallized from an appropriate solvent to give IV. The results are shown in Table I. Analytical and ^{1}H-NMR data are as follows. *Anal.* IVa, Calcd for $C_{17}H_{17}NO$: C, 81.22; H, 6.82; N, 5.99. Found: C, 81.40; H, 7.06; N, 5.64. IVb, Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.19; H, 7.19; N, 5.02. IVc, Calcd for $C_{17}H_{16}N_2O_3$: C, 68.91; H, 5.44; N, 9.45. Found: C, 68.77; H, 5.35; N, 9.28. IVd, Calcd for $C_{17}H_{16}ClNO$: C, 71.45; H, 5.64; N, 4.90. Found: C, 71.41; H, 5.71; N, 4.64. IVe, Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.44; H, 7.49; N, 6.97. IVg, Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.11; H, 6.34; N, 5.81. IVh, Calcd for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.92. Found: C, 68.39; H, 4.99; N, 9.89. ^{1}H-NMR IVa ($CDCl_3$) δ: 2.27 (3H, CH_3, s), 3.70 (2H, CH_2, s) and 9.13 (1H, CHO, s). IVb ($CDCl_3$) δ: 2.27 (3H, CH_3, s), 3.65 (2H, CH_2, s) and 9.26 (1H, CHO, s). IVc (CD_3SOCD_3) δ: 2.22 (3H, CH_3, s), 3.75 (2H, CH_2, s) and 7.78 (1H, β-position, d, J=13 Hz), 9.10 (1H, CHO, s) and 9.35 (1H, NH, d, J=13 Hz). IVd ($CDCl_3$) δ: 2.27 (3H, CH_3, s), 3.62 (2H, CH_2, s) and 9.13 (1H, CHO, s). IVe ($CDCl_3$) δ: 2.30 (3H, CH_3, s), 3.13 (2H, $-CH_2-$, m), 5.05 and 5.08 (each 1H, $=CH_2$, m), 5.80 (1H, $-CH=$, m), 7.23 (1H, β-position, s) and 9.07 (1H, CHO, s). IVg ($CDCl_3$) δ 3.70 (2H, CH_2, s) and 9.18 (1H CHO, s). IVh ($CDCl_3$) δ: 3.72 (2H, CH_2, s) and 9.12 (1H, CHO, s).

Cyclodehydration of I with $AlBr_3$——A mixture of Ia—c (0.01 mol) and $AlBr_3$ (0.03 mol) was heated at 80 °C for 30 min, then 20 ml of 2 N NaOH was added to the mixture. The whole was steam-distilled, and the distillate was treated as usual to give quinolines and anilines. The latter were isolated as their *N*-acetyl derivatives. The yields were as follows. Ia: 6-methylquinoline, 77%; *N*-acetyl-*p*-toluidine, 7%. Ib: quinoline, 57%; acetanilide, 9%. Ic: 6-chloroquinoline, 65%; *N*-acetyl-*p*-chloroaniline, 4%.

Reaction of IV and $AlBr_3$——A mixture of IVa (0.002 mol) and $AlBr_3$ (0.006 mol) was heated at 120—140 °C for 5 h, then 10 ml of H_2O and 20 ml of 2 N NaOH were added. The whole was extracted with ether. The ether layer was dried over K_2CO_3, and concentrated under reduced pressure. The residue was subjected to preparative thin-layer chromatography (silica gel) with benzene–AcOEt (5:1) as a developing solvent to give 0.105 g (37%) of 6-methylquinoline. The same reactions of IVb and of IVd afforded 6-methylquinoline in 52 and 51% yields,

Table I. Hydrolysis of III

	IVa	IVb	IVc	IVd	IVe	IVg	IVh
Amount of III (mol)	0.003	0.01	0.009	0.008	0.0064	0.005	0.005
Amount of H_2O (ml)	5	10	30	10	6	10	10
Amount of EtOH (ml)	15	50	100	50	30	40	20[a]
Refluxing time (min)	60	165	160	165	120	300[b]	300[b]
Recrystallization solvent	Benzene	Benzene	Benzene	Benzene	EtOH	Benzene	Benzene
mp (°C)	167	160	189	166	129	158	160
Yield (%)	75	59	40	48	55	68	65

a) THF (30 ml) was used for dissolution of IIIh.
b) The reaction mixture was heated at 70 °C.

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Table II. Preparation of V by Cyclodehydration of IV with $AlCl_3$

		Va	Vb	Vd	Vg	Vh
Amount of IV (mol)		0.002	0.002	0.002	0.0025	0.002
Reaction temperature (°C)		170—195	190—200	180—200	190—200	140—160
Yield (%)		30	10	27	33	7
Recrystallization solvent			40% Aqueous EtOH	Petroleum ether		Petroleum benzin–CH_2Cl_2
mp (°C)		67.5—68.5[a]	61.5	90—91	67[b]	107—107.5
Analysis (%)	C Calcd		87.41	76.26		72.72
	C (Found)		(87.14)	(75.87)		(72.72)
	H Calcd		6.93	5.27		4.58
	H (Found)		(6.96)	(5.09)		(4.54)
	N Calcd		5.66	5.23		10.60
	N (Found)		(5.57)	(5.18)		(10.59)

The heating time was 5 h in each case.
a) M. Avramoff and Y. Sprinzak [*J. Am. Chem. Soc.*, **78**, 4090 (1956)] reported the melting point of Va to be 67—68 °C.
b) M. Avramoff and Y. Sprinzak [*J. Org. Chem.*, **22**, 571 (1957)] reported the melting point of Vg to be 69—70 °C.

respectively.

Cyclodehydration of IV with $AlCl_3$——A mixture of IV and three equivalents of $AlCl_3$ was heated for 5 h, and made alkaline by the addition of 2 N NaOH. The whole was extracted with ether. The ether layer was dried over K_2CO_3, and concentrated under reduced pressure. The residue was subjected to preparative thin-layer chromatography (silica gel) with benzene–AcOEt (5 : 1) as a developing solvent to give the products. The results are shown in Table II.

Reaction of Nitrobenzene and $AlBr_3$——A solution of 4.00 g (0.015 mol) of $AlBr_3$ in 40 ml of nitrobenzene was heated at 120—140 °C for 6 h, and 50 ml of 2 N HCl was added to the solution. The whole was steam-distilled, and the remaining liquid was made alkaline by the addition of 40% NaOH. The whole was steam-distilled. The distillate was treated as usual to give 0.03 g of *p*-bromoaniline and 0.11 g of 2,4-dibromoaniline.

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