

Synthesis of Amides and Amidines by Reaction of Carboxylic Acids and Amines in the Presence of Polyphosphoric Acid Trimethylsilyl Ester (PPSE)

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(Received January 14, 1986)

The reaction between amines and carboxylic acids in the presence of polyphosphoric acid trimethylsilyl ester (PPSE) has been investigated from the view point of the synthesis of amides and amidines. Benzanilide was selectively prepared from benzoic acid and aniline in the presence of PPSE and pyridine at 100 °C, whereas a mixture of benzanilide and *N,N'*-diphenylbenzamidine was obtained without the use of pyridine. The reaction at 160 °C almost exclusively gave *N,N'*-diphenylbenzamidine. Various symmetrical amidines were obtained from combinations of carboxylic acids and aromatic amines in high yields by simply heating at 160 °C with four molar amounts of PPSE. The reactions of aliphatic and aromatic amines with *N*-monosubstituted and *N,N*-disubstituted amides also afforded corresponding unsymmetrical amidines under the same conditions. The reaction mechanism is discussed in some detail.

Polyphosphoric acid trimethylsilyl ester (PPSE) has been utilized extensively since its first preparation by Imamoto et al.¹⁾ A PPSE-promoted synthesis of heterocyclic compounds²⁾ and nitriles from amides,³⁾ an unusual aldol reaction,⁴⁾ and the Beckmann,¹⁾ pinacol-pinacolone,⁵⁾ and Pummerer rearrangements⁶⁾ have been reported. PPSE is readily prepared from diphosphorus pentaoxide and hexamethyldisiloxane, usually by heating in dichloromethane or chloroform for a short time.^{1,4b)} The structure of this reagent was confirmed to be a mixture of cyclotetraphosphate (1), isocyclotetraphosphate (2), linear tetraphosphate (3), and a small amount of pyrophosphate (4) on the basis of a ³¹P NMR measurement^{2a)} (Scheme 1).

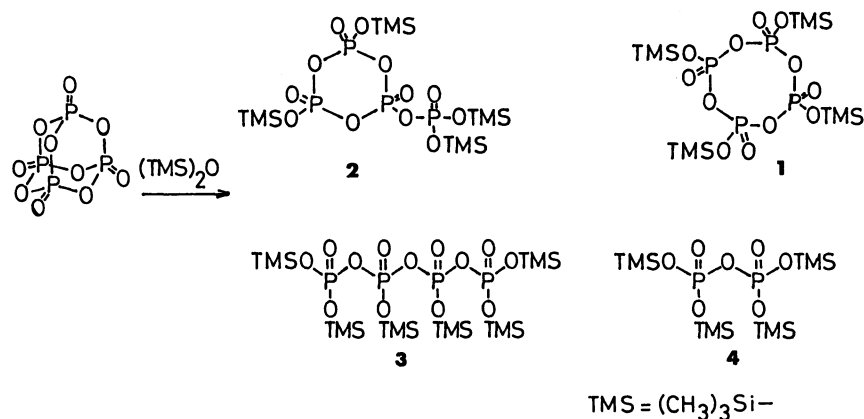
Although polyphosphoric acid (PPA), which has been well-known as a powerful reagent for dehydrative condensations,⁷⁾ is essentially insoluble in organic solvents, PPSE is readily soluble in various aprotic solvents such as benzene, chlorinated hydrocarbons, and sulfolane. Therefore, PPSE should be accepted as a very applicable reagent for an organic synthesis, compared with PPA. The structural and

characteristic reactions of PPSE are similar to those of polyphosphoric acid ethyl ester (PPE),⁸⁾ of which a number of reactions have been presented mainly, from the view point of dehydration reactions.⁹⁾ In a comparison of these two polyphosphoric acid ester reagents, PPSE can be prepared much easier than PPE, whose preparation requires a few days from diphosphorus pentaoxide and diethyl ether.⁸⁾ Furthermore, PPSE was more reactive than PPE in some reactions.^{2,4,7)}

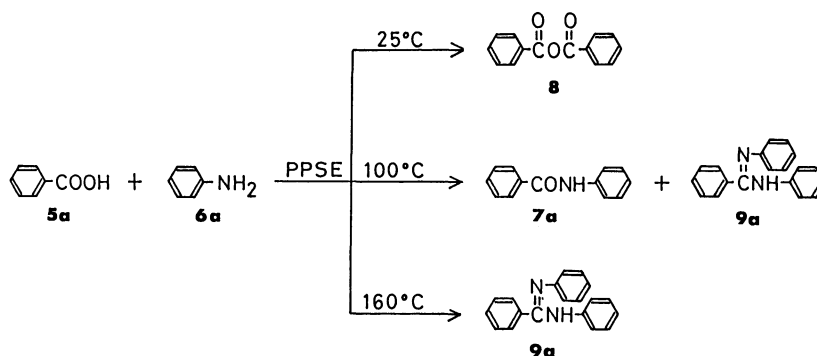
It has been demonstrated that a number of heterocyclic compounds can be easily prepared from appropriate amino compounds and carboxylic acids using PPA, PPE, and PPSE. On the other hand, the reactions of simple carboxylic acids with amines to afford acyclic compounds were only sparingly reported.^{9a)} Here, we wish to report on a novel synthesis of amides and amidines by a reaction of carboxylic acids and amines in the presence of PPSE.

Results and Discussion

Synthesis of Amides from Carboxylic Acids and



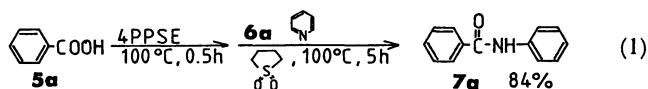
Scheme 1.



Scheme 2.

Amines. Our initial object was a synthesis of amides **7** by a direct condensation of carboxylic acids **5** and amines **6** using PPSE as condensing agent. In the beginning, the reaction between benzoic acid (**5a**) and aniline (**6a**) was conducted at the various temperatures as illustrated in Scheme 2. Results of the reactions are summarized as follows: 1) Benzoic anhydride (**8**) was the major product at 25 °C. 2) A mixture of almost the same amount of benzanilide (**7a**) and *N,N'*-diphenylbenzamidine (**9a**) was obtained at 100 °C. 3) Amidine **9a** was the only product at 160 °C.

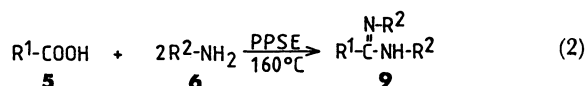
The synthesis of amidines at a high temperature will be discussed later. For the purpose of a selective formation of amide **7a**, pyridine, which should increase the nucleophilicity of aniline (**6a**), was added to the reaction system. The procedure of the amide-forming reaction was examined. Thus, 1) an equimolar amount of benzoic acid (**5a**), aniline (**6a**), and pyridine were added to four-fold molar amounts of PPSE dissolved in sulfolane at 100 °C. 2) In the first step, **5a** was treated in a PPSE solution of sulfolane for 30 min at 100 °C, and then **6a** and pyridine were added to the solution. 3) A mixture of **5a** and pyridine in a small amount of 1,2-dichloroethane was added to PPSE solution in sulfolane at 100 °C, and then **6a** was added to the solution. The yields of amide **7a** by the each procedure were 80, 84, and 49%, respectively. The reaction was also carried out in various solvents such as sulfolane, anisole, dichloromethane, and *N,N*-dimethylacetamide, and sulfolane was found to be the best solvent for this reaction (Eq. 1).



Although a detailed search was made to establish the optimum reaction conditions for amide formation, the suppression of the side reactions of amidine formation was fairly difficult. Therefore, it was concluded that this method was not so generally applicable compared with a direct synthesis of

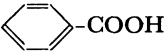
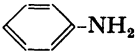
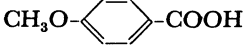
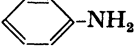
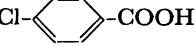
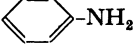
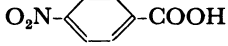
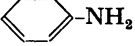
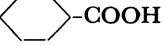
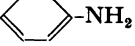
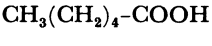
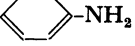
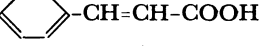
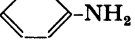
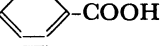
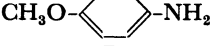
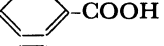
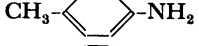
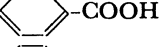
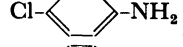
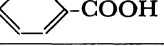
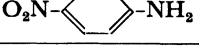
amides by the condensations of carboxylic acids with amines using some condensing agents.

Synthesis of Symmetrical Amidines from Carboxylic Acids and Amines.¹⁰ The results of the high-temperature reaction described above have led to the suggestion that the reaction of carboxylic acids **5** with amines **6** in the presence of PPSE would be generalized to a direct synthesis of symmetrical amidines **9** as illustrated in Eq. 2. To our knowledge, the conversion of carboxylic acids and amines to amidines has been unknown except the case of cyclic amidines.¹¹



Various examples of the synthesis of symmetrical amidines are summarized in Table 1. From Entry 1 to 7, a variety of carboxylic acids **5** were treated with two equivalents of aniline (**6a**) at 160 °C for 5 h without solvent. From Entry 8 to 11, benzoic acid (**5a**) with aromatic amines **6** were examined. *N,N'*-Diphenylamidines were obtained by a reaction between aniline (**6a**) and various aromatic, aliphatic, and α,β -unsaturated carboxylic acids in high yields. *N,N'*-Bis(*p*-nitrophenyl)benzamidine (**9k**) was obtained from benzoic acid and *p*-nitroaniline having low nucleophilicity by use of PPSE prepared from two equivalents of hexamethyldisiloxane (Entry 11). When PPSE prepared from diphosphorus pentaoxide and three equivalents of hexamethyldisiloxane was used, the reaction of the same starting compounds did not afford the corresponding amidine **9k** but gave *N*-(*p*-nitrophenyl)benzamide in 59% yield. It was observed by a measurement of the ³¹P NMR spectra that the PPSE prepared by the former method contained a large amount of isocyclotetraphosphate **2** having an active blanchet unit structure.^{2a} Thus, even from nitroaniline with a low nucleophilicity, amidine **9k** can be obtained using the active PPSE. Contrary to the successful synthesis of *N,N'*-diaryl-substituted amidines **9** from aromatic amines possessing electron-donating and -withdrawing groups,

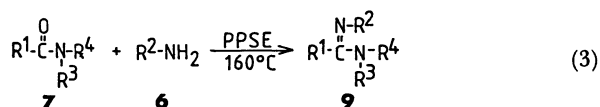
Table 1. Preparation of Symmetrical Amidines

Entry	Carboxylic acid	Amine	Amidine		
			Code	Yield/% ^{a)}	Mp(θ_m /°C) (lit.) ^{b)}
1			9a	83	143—144 (144 ¹³⁾)
2			9b	87	115—116 (107—108 ¹⁴⁾)
3			9c	88	149—150 (149 ¹⁵⁾)
4			9d	84	151—153 (155 ¹⁶⁾)
5			9e	81	110—111
6			9f	79	91—92 (90 ¹⁷⁾)
7			9g	65	115.5—116.5
8			9h	88	120—122 (125 ¹⁸⁾)
9			9i	87	131—131.5
10			9j	69	140—141
11			9k	82	193—194.5

a) Yields are after recrystallized from aqueous ethanol. b) Melting points are uncorrected.

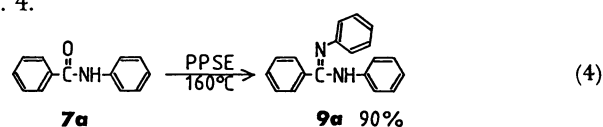
highly nucleophilic aliphatic amines gave a mixture of amidines **9** and amides **7** in low yields.

Synthesis of Unsymmetrical Amidines from Amides and Amines. In the course of the reaction between carboxylic acids **5** and aromatic amines **6**, interesting phenomena were observed. When an equimolar amount of benzoic acid (**5a**) and aniline (**6a**) were reacted in the presence of PPSE at 160 °C for 5 h, amidine **9a** was obtained in 82% yield based on aniline, and benzanilide (**7a**) was not isolated from the reaction mixture. This result suggests that the rate of formation of amidine **9a** from **7a** should be greater than the rate of formation of benzanilide (**7a**), if the intermediate to give **9a** is **7a**. To prove the reaction pathway, the reaction of benzanilide (**7a**) and aniline (**6a**) was conducted. *N,N'*-Diphenylbenzamidine (**9a**) was also obtained in 90% yield under the same conditions for the amidine formation described above. Therefore, this reaction was successfully extended to an unsymmetrical amidine synthesis as illustrated in Eq. 3.



As summarized in Table 2, various examples of the reaction were conducted. It is interesting to note that aliphatic amines, as well as aromatic amines could be applicable in this reaction, giving moderate to excellent yields of amidines **9**, whereas aliphatic

amines did not give satisfactory results in a direct synthesis of the symmetrical amidines mentioned earlier. Primary, secondary, and tertiary aliphatic amines were examined in the reaction with benzanilide (**7a**). Amidine **9o** was obtained in moderate yield from cyclohexylamine, while the product of the reaction with hexylamine was a mixture of the desired amidine **9n** and *N,N'*-diphenylbenzamidine (**9a**). In the reaction with *t*-butylamine, the amine did not react with benzanilide (**7a**) and **9a** was obtained in 87% yield based on **7a**. Amide **7a** was expected to dimerize through the reaction to give amidine **9a**, similar to the reaction of amides with PPE.^{9b} Indeed, amine **7a** afforded amidine **9a** in 90% yield by simply heating at 160 °C with excess of PPSE as depicted in Eq. 4.



Furthermore, not only *N*-monosubstituted amides but also *N,N*-disubstituted amides could be used for this type of reaction. When the reaction of benzamide **7b** was conducted, it was found that **7b** reacted with PPSE predominantly to afford *p*-methoxybenzonitrile.^{3b}

Reaction Mechanism. When one discusses the mechanism of the present reaction, PPSE has two possible roles, where it acts as a silylating agent and a phosphorylating agent. Because tris(trimethylsilyl) orthophosphate, whose trimethylsilyl function seems

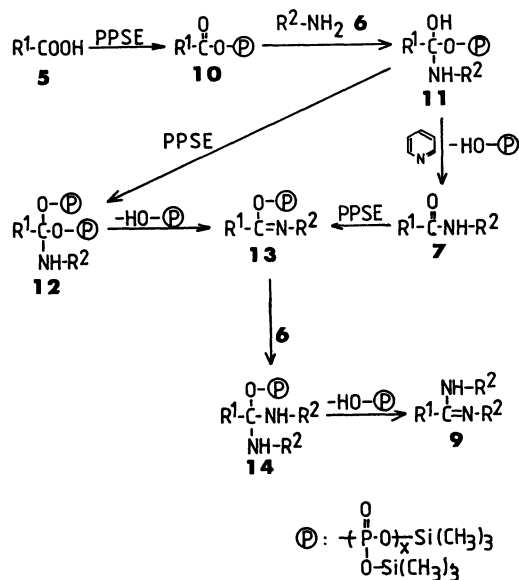
Table 2. Preparation of Unsymmetrical Amidines

Entry	Amide	Amine	Amidine		
			Code	Yield/%	Mp (Bp/Torr) /°C (lit.)
1				9l	97 ^{a)} 108—110 ^{b)} (120 ¹⁹⁾)
2				9m	91 ^{a)} 181—183 ^{b)} (184 ²⁰⁾)
3				9n	23 ^{d)} —
			+		
				9a	53 ^{d)} —
4				9o	54 ^{a)} 142—143.5 ^{b)}
5				9a	87 ^{a)} —
6				9p	94 ^{a)} 126—128 ^{b)} (135—136 ²¹⁾)
7				9q	89 (120/0.1) ^{c)} (75—76/0.005 ²²⁾)
8				9r	85 (140/0.1) ^{c)} (90/0.01 ²³⁾)

a) Yields are after recrystallized from aqueous ethanol. b) Melting points are uncorrected. c) Boiling points refer to the bath temperature of bulb to bulb distillation. d) Yields are calculated from integration of ¹H NMR spectrum of the mixture of **9a** and **9a**. e) 1 Torr=133.322 Pa.

to possess almost the same reactivity as PPSE was found to be ineffective for amidine synthesis, it is concluded that phosphorylation of carboxylic acid by PPSE is the initial reaction. The mechanism is presumed as illustrated in Scheme 3. In the beginning, carboxylic acid **5** reacts with PPSE to afford mixed anhydride **10**. Amide **7** is obtained by the action of pyridine through intermediate **11**, which is produced by the reaction of **10** and amine **6**. Intermediate **11** is then phosphorylated with PPSE to afford **12**. Imidate intermediate **13** is produced by the elimination of phosphoric function from **12**. Alter-

natively, amide **7** is converted to **13** by the reaction with PPSE. Finally, **13** reacts with amine **6** to afford amidine **9**. Although amine **6** can react with PPSE, the reaction product (phosphoric amide and/or phosphoric acid salt of **6**) should decompose at a high temperature to liberate amine **6**, and **6** may react with **13**. Since aromatic amine should be liberated more readily than aliphatic amine at a high temperature, the reaction proceeds predominantly with aromatic amine. The reaction between benzoic acid (**5a**) and an equimolar amount of aniline (**6a**) in the presence of PPSE afforded amidine **9a** in 82% yield



Scheme 3.

based on **6a**. This result suggests that the reaction from **13** to **9** was faster than the reaction from **10** to **13**. In the reaction of amide **7a** and aliphatic amine, the only successful example was the case of cyclohexylamine. Therein, hexylamine which has high nucleophilicity should competitively react with **13** and PPSE existing in the reaction mixture, and *t*-butylamine could not attack **13** because of the steric hindrance.

Conclusion

The conventional starting materials for amidine synthesis¹⁰ are nitriles, imidates, imidoalides, and orthoesters etc., which are essentially derivatives of carboxylic acids and/or amines. The present method offers a convenient synthesis of amidines. Thus, symmetrical and unsymmetrical amidines were synthesized directly from reactant pairs of carboxylic acid-amine and amide-amine, respectively, in the presence of PPSE. Since PPSE possesses the characteristics of a Lewis acid as well as a dehydration agent, it should be accepted as a unique reagent for dehydrative condensation reactions.

Experimental

The ¹H NMR spectra were determined with a JEOL C-60 HL, and the chemical shifts are given in ppm based on tetramethylsilane. The ³¹P NMR spectra were recorded with a JEOL FX-100. Solvents such as dichloromethane were purified by the usual procedures.

Preparation of Polyphosphoric Acid Trimethylsilyl Ester (PPSE). In a 50 mL round-bottom flask, a mixture of 1.42 g (5 mmol) of diphosphorus pentaoxide, 2.56 g (16 mmol) of hexamethyldisiloxane and 3 mL of dichloromethane was heated at refluxing temperature for 30 min

under a thin stream of nitrogen. After a distillation apparatus was equipped on the flask, the mixture was gradually heated to 160 °C under nitrogen. During this period, volatile compounds such as dichloromethane and excess hexamethyldisiloxane were distilled away. The residual viscous syrup was used for the following reactions.

Preparation of Benzanilide (7a). To the syrup of PPSE which was prepared from 10 mmol of diphosphorus pentaoxide and 20 mmol of hexamethyldisiloxane, 5 mL of sulfolane and 0.305 g (2.5 mmol) of benzoic acid (**5a**) were added. After the solution was stirred for 30 min, 0.2 mL (2.5 mmol) of pyridine and 0.233 g (2.5 mmol) of aniline (**6a**) were added. The reaction mixture was stirred for 5 h at 100 °C under nitrogen. The benzanilide (**7a**) was obtained by pouring the mixture into cold 1 M[†] NaOH solution. Yields was 0.392 g (84%); Mp 160–161 °C (161 °C¹²); IR (KBr) 3300 cm⁻¹ (N-H), 1650 cm⁻¹ (C=O), 1594 and 1485 cm⁻¹ (aromatic).

General Procedure for the Preparation of Symmetrical Amidines (9a–k). To the syrup of PPSE which was prepared from 5 mmol of diphosphorus pentaoxide and 16 mmol of hexamethyldisiloxane, 1.25 mmol of carboxylic acid and 2.50 mmol of amine were added at 160 °C, and the solution was stirred for 5 h at the temperature under nitrogen. The crude product was isolated by pouring the reaction mixture into a 1 M NaOH solution. Recrystallization from aqueous ethanol gave pure symmetrical amidine.

The yield and melting points of the products are summarized in Table 1. The IR and NMR data of the amidines are given in Table 3.

General Procedure for the Preparation of Amidines (9l–r) from Amides 7 and Amines 6. To the syrup of PPSE which was prepared from 10 mmol of diphosphorus pentaoxide and 20 mmol of hexamethyldisiloxane, 2.5 mmol of amide and 2.5 mmol of amine were added at 160 °C. The mixture was stirred for 2 h at that temperature under nitrogen. The product was isolated by pouring the reaction mixture into a 1 M NaOH solution. The pure amidine was obtained by recrystallization from aqueous ethanol.

Yields and melting points are summarized in Table 2. The IR and NMR data of the products are also given in Table 3. Analytical data of new compounds are shown in Table 4.

Reaction of Benzanilide (7a) and Hexylamine. To the syrup of PPSE, 0.591 g (3 mmol) of benzanilide (**7a**) and 0.303 g (3 mmol) of hexylamine were added at 160 °C. After the reaction was carried out as described above, the reaction mixture was poured into a 1 M NaOH solution. The solution was extracted by dichloromethane, dried over MgSO₄, and the solvent was evaporated. Thin-layer chromatogram (aluminum oxide, ethyl acetate/hexane=1/10) showed two spots at *R_f* 0.58 and 0.51. The latter spot was the same *R_f* value of amidine **9a**. The mixture of these two spots, collected by column chromatography (aluminum oxide, ethyl acetate/hexane=1/10), weighed 0.414 g and shows the following spectra: IR (KBr) 1620 cm⁻¹ (C=N), 1585 cm⁻¹ (aromatic), and 1220 cm⁻¹ (C–N), ¹H NMR (CDCl₃) δ=0.70–1.85 and 6.50–8.00 (integration

[†] 1 M=1 mol dm⁻³.

Table 3. Spectral Data of Amidines

Amidine	IR C=N/cm ⁻¹	¹ H NMR/ δ ppm (CDCl ₃)
9a	1620	5.58(s, 1H), 6.68—7.55(m, 15H)
9b	1625	3.67(s, 3H), 5.70(s, 1H), 6.50—7.50(m, 14H)
9c	1625	6.63—7.53(m)
9d	1640	6.62—8.42(m)
9e	1635	0.86—2.90(m, 11H), 5.80(s, 1H), 6.75—7.49(m, 10H)
9f	1630	0.56—2.43(m, 11H), 6.62—7.47(m, 11H)
9g	1635	6.33(s, 1H), 6.60(s, 1H), 6.72—7.42(m, 16H)
9h	1625	3.63(s, 3H), 5.70(s, 1H), 6.34—7.42(m, 16H)
9i	1625	2.22(s, 3H), 6.13—7.79(m, 14H)
9j	1625	6.57—7.52(m)
9k	1635	6.64—8.31(m)
9l	1620	3.65(d, 3H), 6.33—7.87(m, 14H)
9m	1620	6.77—8.20(m)
9o	1620	0.93—2.22(m, 11H), 5.86(s, 1H), 6.55—7.85(m, 10H)
9p	1605	3.00(s, 3H), 4.61(s, 1H), 6.50—7.83(m, 10H)
9q	1615	1.83(s, 3H), 3.00(s, 6H), 6.65—7.52(m, 5H)
9r	1635	1.64—2.60(m, 4H), 2.85(s, 3H), 3.35(t, 2H), 6.63—7.57(m, 5H)

Table 4. Analytical Data of New Compounds

Code	Found/%	Calculated/%
9e	C: 82.31, H: 8.05, N: 9.94	C ₁₉ H ₂₂ N ₂ ; C: 81.97, H: 7.97, N: 10.06
9g	C: 84.80, H: 6.10, N: 9.23	C ₂₁ H ₁₈ N ₂ ; C: 84.53, H: 6.08, N: 9.39
9i	C: 83.67, H: 6.68, N: 9.05	C ₂₁ H ₂₀ N ₂ ; C: 83.96, H: 6.71, N: 9.33
9j	C: 66.86, H: 4.02, N: 8.01, Cl: 20.70	C ₁₉ H ₁₄ N ₂ Cl ₂ ; C: 66.88, H: 4.14, N: 8.21, Cl: 20.78
9k	C: 62.82, H: 3.96, N: 15.89	C ₁₉ H ₁₄ N ₄ O ₄ ; C: 62.98, H: 3.89, N: 15.46
9o	C: 82.05, H: 8.07, N: 9.79	C ₁₉ H ₂₂ N ₂ ; C: 81.97, H: 7.97, N: 10.06

ratio was 2.1:1). From these spectra data the product was the mixture of amidine **9n** and **9a** in the yield of 23 and 53%, respectively.

References

- 1) T. Imamoto, H. Yokoyama, and M. Yokoyama, *Tetrahedron Lett.*, **22**, 1803 (1981).
- 2) a) K. Yamamoto and H. Watanabe, *Chem. Lett.*, **1982**, 1225; b) Y. Imai, A. Mochizuki, and M. Kakimoto, *Synthesis*, **1983**, 851.
- 3) M. Yokoyama, S. Yoshida, and T. Imamoto, *Synthesis*, **1982**, 591.
- 4) a) T. Imamoto, H. Yokoyama, and M. Yokoyama, *Tetrahedron Lett.*, **23**, 1467 (1982); b) T. Imamoto, T. Matsumoto, H. Yokoyama, M. Yokoyama, and K. Yamaguchi, *J. Org. Chem.*, **49**, 1105 (1984).
- 5) M. Kakimoto, Y. Imai, unpublished data.
- 6) M. Kakimoto and Y. Imai, *Chem. Lett.*, **1984**, 1831.
- 7) For reviews, see: a) F. D. Popp and W. E. McEwen, *Chem. Rev.*, **58**, 321 (1958); b) F. Uhlig and H. R. Snyder, *Adv. Org. Chem.*, **1**, 35 (1960).
- 8) K. Langheld, *Chem. Ber.*, **43**, 1857 (1910).
- 9) a) Y. Kanaoka, O. Yonemitsu, K. Tanizawa, and Y. Ban, *Chem. Pharm. Bull.*, **12**, 773 (1964); b) Y. Kanaoka, E. Sato, O. Yonemitsu, and Y. Ban, *Tetrahedron Lett.*, **1964**, 2419; c) Y. Kanaoka, M. Machida, O. Yonemitsu, and Y. Ban, *Chem. Pharm. Bull.*, **13**, 1065 (1965); d) Y. Kanaoka, Y. Ban, K. Miyashita, and K. Irie, *ibid.*, **14**, 934 (1966); e) Y. Kanaoka, E. Sato, and Y. Ban, *ibid.*, **15**, 101 (1967); f) Y. Kanaoka, K. Tanizawa, E. Sato, O. Yonemitsu, and Y. Ban, *ibid.*, **15**, 593 (1967); g) Y. Kanaoka, O. Yonemitsu, and E. Sato, *ibid.*, **16**, 280 (1968); h) Y. Kanaoka, E. Sato, and O. Yonemitsu, *Tetrahedron*, **24**, 2591 (1968); i) Y. Kanaoka, O. Yonemitsu, and K. Tanizawa, *ibid.*, **17**, 2381 (1969); j) O. Yonemitsu, K. Miyashita, Y. Ban, and Y. Kanaoka, *Tetrahedron*, **25**, 95 (1969); k) Y. Kanaoka, K. Miyashita, and O. Yonemitsu, *ibid.*, **25**, 2757 (1969); l) M. P. Cava, M. V. Lakshmikantham, and M. J. Mitchell, *J. Org. Chem.*, **34**, 2665 (1969); m) Y. Kanaoka, T. Kuga, and K. Tanizawa, *Chem. Pharm. Bull.*, **18**, 397 (1970); n) J. H. Adams, J. R. Lewis, and J. G. Paul, *Synthesis*, **1979**, 429; o) M. Yokoyama, M. Nakamura, S. Imanoto, and K. Yamaguchi, *J. Chem. Soc., Chem. Commun.*, **1981**, 560; p) M. Yokoyama, M. Nakamura, H. Ohtaki, and T. Imamoto, *J. Org. Chem.*, **47**, 1090 (1982); q) T. Imamoto, M. Kodaera, and M. Yokoyama, *Bull. Chem. Soc. Jpn.*, **55**, 2303 (1982); r) T. Imamoto, M. Kodaera, and M. Yokoyama, *Synthesis*, **1982**, 134; s) T. Imamoto, T. Takaoka, and M. Yokoyama, *ibid.*, **1983**, 142.
- 10) M. Kakimoto, S. Ogata, A. Mochizuki, and Y. Imai, *Chem. Lett.*, **1984**, 821.
- 11) A. Gautier, M. Miocque, C. C. Farnoux, "The Chemistry of Amidines and Imidates," ed by S. Patai, John

Wiley & Sons (1975), p. 283.

12) C. N. Webb, *Org. Syn.*, Coll. Vol. I., 82 (1941).

13) D. N. Shigotin and T. K. Syrkin, *Zh. Fiz. Khim.*, **23**, 241 (1949).

14) M. W. Parteidge, *J. Chem. Soc.*, **1949**, 3043.

15) S. A. Kulkarui and R. C. Shah, *J. Indian Chem. Soc.*, **27**, 111 (1950).

16) R. C. Shahm, *J. Univ. Barmay*, **1936**, 5, pt. 2, 62.

17) N. S. Drozdov and A. F. Bekhli, *J. Gen. Chem.*, **14**, 280 (1944).

18) N. J. Sintiv, J. S. Rodia, J. A. Tursich, H. L. Davis, and G. L. Webster, *J. Am. Chem. Soc.*, **71**, 3990 (1949).

19) T. B. Desai and R. C. Shah, *J. Indian Chem. Soc.*, **26**, 121 (1949).

20) C. Chew, F. L. Pyman, *J. Chem. Soc.*, **1927**, 2318.

21) E. L. Pyman, *J. Chem. Soc.*, **123**, 367 (1923).

22) H. Brederock, R. Gompper, K. Klemm, and H. Rempfer, *Chem. Ber.*, **92**, 837 (1959).

23) H. Brederock and K. Brederock, *Chem. Ber.*, **94**, 2278 (1961).
