

Synthesis and Characterization of Aromatic Polyamides Derived from New Phenylated Aromatic Diamines

Yoshimitsu SAKAGUCHI* and Frank W. HARRIS

*Department of Polymer Science, The University of Akron,
Akron, OH44325, U.S.A.*

(Received May 8, 1992)

ABSTRACT: Four new phenylated aromatic diamines, 1,4-bis(4-amino-3,5-diphenylphenyl)benzene (**1a**), 1,3-bis(4-amino-3,5-diphenylphenyl)benzene (**1b**), 1,4-bis(4-aminophenyl)-2,3,5-triphenylbenzene (**2a**), and 1,4-bis(4-aminophenyl)-2,3,5,6-tetraphenylbenzene (**2b**) were synthesized and polymerized with terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC). All the polyamides showed high thermal stability with 5% weight-loss temperatures in the range of 466—524°C in air or nitrogen, and no melting peak below their decomposition temperatures. The polymers containing *m*-catenation had glass transition temperatures in the range of 275—349°C, and were soluble in *N*-methyl-2-pyrrolidone (NMP). The rigid rod-like polyamides consisting all *para*-oriented linkages showed no clear glass transition. In the rod-like polymers, polymer **2a**/TPC showed good solubility in NMP, and preliminary optical microscope observation for the 20% solution showed an anisotropic property.

KEY WORDS Aromatic Polyamide / Phenyl Substituent / Phenylated Aromatic Diamine / Thermal Stability / Solubility / Rigid-Rod / Optical Anisotropy /

Aromatic polyamides, such as poly(*para*-phenylene terephthalamide), show excellent mechanical properties and good thermal properties. However, these polymers are infusible and show limited solubility in organic solvents. There are general concepts for structural modification to improve the solubility of polymers as follows: introduction of flexible or kinked structure, decrease of structural regularity and symmetry, and incorporation of side chains or bulky substituents. To increase the solubility while maintaining the thermal stability, the structural modification with whole aromatic system is particularly preferred.¹⁻¹⁰ From this view point, the introduction of phenyl side groups into the polymer chain is considered as an effective approach. In the case of aromatic rigid rod-like polyamides, several polymers having

aromatic substituents were reported to be soluble in organic solvents,¹¹⁻¹⁴ and display anisotropic properties.¹¹⁻¹³ An advantage to obtain a soluble rigid rod-like polyamide lies in its possible application to the reinforcing material in molecular composite as well as the high-strength and high-modulus fiber.

The authors reported the preparation of two new series of phenylated aromatic diamines and polymerization of polyimides derived from these diamines.¹⁵ This report shows the synthesis of new aromatic polyamides by the polymerization of these phenylated diamines and diacid chlorides, and some characterizations of the polymers obtained. The details of the preparation of these diamines are also described.

* Present address: Toyobo Research Center, Toyobo Co., Ltd., 1-1 Katata 2-chome, Ohtsu, 520-02, Japan.

EXPERIMENTAL

Materials

N-Methyl-2-pyrrolidone (NMP) was distilled over P₂O₅ under reduced pressure. Terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were distilled under reduced pressure. Other chemicals were used without further purification.

Monomer Synthesis

1,4-Bis(1,3-dibenzoyl-2-propyl)benzene (3a). Terephthalaldicarboxaldehyde (28.4 g, 0.212 mol) and acetophenone (152.1 g, 1.27 mol) were dissolved in 700 ml of 95% ethanol. Potassium hydroxide (29.6 g, 0.528 mol) in 32 ml of water was added to the solution dropwise. A precipitate appeared soon. The reaction mixture was stirred and refluxed for 3 hours, then filtered. The solid obtained was washed with 500 ml of fresh 95% ethanol under reflux; Yield 11 g (93%). mp 184–192°C (lit.¹⁶ 204–205°C). ¹H NMR (CDCl₃) δ = 3.6 (d, 8H, CH₂), 4.2 (m, 2H, CH), 7.4–7.8 (m, 16H, aromatic H), 8.2 ppm (m, 8H, aromatic H).

1,4-Phenylenebis-γ,γ'-(2',6'-diphenylpyrylium)tetrafluoroborate (4a). Triphenylmethanol (113.4 g, 0.436 mol) was dissolved in 700 ml of acetic anhydride at 65°C, then the solution was cooled to room temperature with a water bath. 49% Fluoboric acid (78.0 g, 0.435 mol) was added dropwise maintaining the reaction at room temperature. Then, **3a** (90.0 g, 0.156 mol) was added, and the resulting suspension was stirred for 17 hours. The product was collected, washed with THF several times, and then dried; Yield 106 g (96%).

1,4-Bis(4-nitro-3,5-diphenylphenyl)benzene (5a). Nitromethane (236 g, 3.86 mol) was added to a solution of potassium (15.5 g, 0.396 mol) in 580 ml of *tert*-butanol. This solution was added to a stirred suspension of **4a** (100 g, 0.140 mol) in 580 ml of *tert*-butanol. Another solution of potassium (15.5 g, 0.396 mol) in 580 ml of *tert*-butanol was added, then the mixture was stirred under reflux for 2 hours.

The precipitate was collected, stirred in hot water, filtered, and dried; Yield 64.5 g (74%). After the recrystallization from dioxane–ethanol (4:1), the needles obtained showed the melting point at 341–344°C; IR (KBr) 1360 and 1530 cm⁻¹ (NO₂). Anal. Calcd for C₄₂H₂₈N₂O₄: C, 80.75%; H, 4.52%; N, 4.48%. Found: C, 80.37%; H, 4.73%; N, 4.36%.

1,4-Bis(4-amino-3,5-diphenylphenyl)benzene (1a). A suspension of **5a** (12.0 g, 0.0192 mol) in 600 ml of 2-methoxyethanol was stirred and heated to 100°C. Stannous chloride (48.7 g, 0.216 mol) which was dissolved in 115 ml of hydrochloric acid was added to the suspension. After stirred around 100°C for 5 hours, the same amount of stannous chloride solution was added, and the reaction was continued for another 15 hours. The reaction mixture was poured into 1000 ml of water and filtered. The solid obtained was neutralized by ammonium hydroxide, washed with water, and dried; Yield 10.6 g (97%). The crude product was recrystallized from xylene several times; mp 310–312°C. IR (KBr) 3360 and 3450 cm⁻¹ (NH). Anal. Calcd for C₄₂H₃₂N₂: C, 89.33%; H, 5.71%; N, 4.96%. Found: C, 89.52%; H, 5.76%; N, 4.71%.

1,3-Bis(1,3-dibenzoyl-2-propyl)benzene (3b). The reaction between isophthalaldicarboxaldehyde and acetophenone was carried out following a similar procedure with the preparation of **3a**. During the reaction, two phases separated. The lower layer, which was viscous and dark brown, was separated and stirred with ethanol. After the ethanol was removed by decantation, the viscous residue was dried; Yield 77%. ¹H NMR (CDCl₃) δ = 3.3 (d, 8H, CH₂), 4.0 (m, 2H, CH), 6.4–7.9 ppm (m, 24H, aromatic H).

1,3-Phenylenebis-γ,γ'-(2,6-diphenylpyrylium)tetrafluoroborate (4b). The procedure used in the preparation of **4a** was applied to that of **4b**; Yield 35%.

1,3-Bis(4-nitro-3,5-diphenylphenyl)benzene (5b). A similar procedure with the preparation

of **5a** was applied to that of **5b**. After the reaction, water was added to the reaction mixture. The precipitate was collected and dried; Yield 92%. mp 250–258°C. IR (KBr) 1360 and 1530 cm^{-1} (NO_2).

1,3-Bis(4-amino-3,5-diphenylphenyl)benzene (1b). The procedure used in the preparation of **1a** was applied to that of **1b**; Yield 97%. The crude product was recrystallized from toluene/ethanol. mp 212–213°C. IR (KBr) 3380 and 3480 cm^{-1} (NH_2). *Anal.* Calcd for $\text{C}_{42}\text{H}_{32}\text{N}_2$: C, 89.33%; H, 5.71%; N, 4.96%. Found: C, 89.78%; H, 5.70%; N, 4.71%.

1,3-Bis(4-nitrophenyl)acetone (7). 4-Nitrophenylacetic acid (**6**) (100 g, 0.552 mol) was dissolved in 600 ml of acetic anhydride. Keeping the system at 80°C, 300 ml (2.16 mol) of triethylamine was added dropwise and the solution was stirred for 2 hours. The solution was poured into 1000 ml of 10% hydrochloric acid and filtered. The solid obtained was ground into a powder, and stirred in 500 ml of refluxing concentrated hydrochloric acid for 8 hours. The product was collected and washed with water several times; Yield 79.8 g (96%). IR (KBr) 1340 and 1520 cm^{-1} (NO_2), 1720 cm^{-1} ($\text{C}=\text{O}$). ^1H NMR (CDCl_3) δ =8.0, 7.3 (dd, J =8 Hz, aromatic H), 4.0 ppm (s, 4H, CH_2).

2,5-Bis(4-nitrophenyl)-3,4-diphenylcyclopentadienone (8). Benzil (54.6 g, 0.260 mol) and **7** (78.0 g, 0.260 mol) were added to 390 ml of ethanol. After the stirred solution was heated nearly to the boiling point, a solution of 7.8 g (0.139 mol) of potassium hydroxide in 40 ml of ethanol was added slowly. The reaction mixture was stirred for 1 hour, and then allowed to cool to room temperature. The product was collected and washed with ethanol several times; Yield 44 g (36%). IR (KBr) 1340 and 1510 cm^{-1} (NO_2), 1715 cm^{-1} ($\text{C}=\text{O}$).

1,4-Bis(4-nitrophenyl)-2,3,5-triphenylbenzene (9a). Phenylacetylene (19.3 g, 0.189 mol), **8** (30.0 g, 0.063 mol) and 130 ml of *o*-dichlorobenzene was stirred at 180°C for two hours. The reaction mixture was allowed to

cool to room temperature, and poured into 500 ml of hexane. The product was collected by filtration and dried; Yield 22.9 g (66%).

1,4-Bis(4-aminophenyl)-2,3,5-triphenylbenzene (2a). A solution of **9a** (20.0 g, 0.0365 mol) in 250 ml of 2-methoxyethanol was stirred and heated to 80°C. A solution of stannous chloride (82.2 g, 0.364 mol) in 130 ml of hydrochloric acid was added. Thereafter, the mixture was stirred around 100°C for 5 hours. The reaction mixture was allowed to cool to room temperature, and poured into 600 ml of water and filtered. The solid obtained was neutralized by ammonium hydroxide, washed with water, and dried; Yield 10.0 g (61%). The crude product was recrystallized from toluene; mp 256–258°C. IR (KBr) 3460 and 3480 cm^{-1} (NH_2). ^1H NMR (CDCl_3) δ =3.3 (s, 4H, NH_2), 6.0–7.3 ppm (m, 24H, aromatic H). *Anal.* Calcd for $\text{C}_{36}\text{H}_{28}\text{N}_2$: C, 88.49%; H, 5.78%; N, 5.73%. Found: C, 88.85%; H, 5.83%; N, 5.58%.

1,4-Bis(4-nitrophenyl)-2,3,5,6-tetraphenylbenzene (9b). The procedure used in the preparation of **9a** was applied to that of **9b**, except the reaction time was extended to 17 hours; Yield 63%.

1,4-Bis(4-aminophenyl)-2,3,5,6-tetraphenylbenzene (2b). The procedure used in the preparation of **2a** was applied to that of **2b**; Yield 45%. The crude product was recrystallized from pyridine; mp 453°C (DSC). IR (KBr) 3380 and 3450 cm^{-1} (NH_2). *Anal.* Calcd for $\text{C}_{42}\text{H}_{32}\text{N}_2$: C, 89.33%; H, 5.71%; N, 4.96%. Found: C, 88.54%; H, 5.64%; N, 4.92%.

Polymerization

As an example, the polymerization of **2a** and terephthaloyl chloride (TPC) is shown below.

In a 25 ml of three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a drying tube were placed **2a** (0.4000 g, 0.8187 mol) and 2.9 g of NMP. After the system was cooled below 5°C with an ice bath, TPC (0.1662 g, 0.8186 mol) was added and stirred

for 30 min. Thereafter, the reaction was continued at room temperature for 15 hours. The polymer solution was poured into 500 ml of methanol. The polymer precipitated was collected and dried.

The other polymers were synthesized similarly. The polymerization concentrations were selected between 5% and 20%. When lithium carbonate or lithium chloride was added in the polymerization system, an equivalent with the amide linkages was added after the addition of the monomers.

Measurements

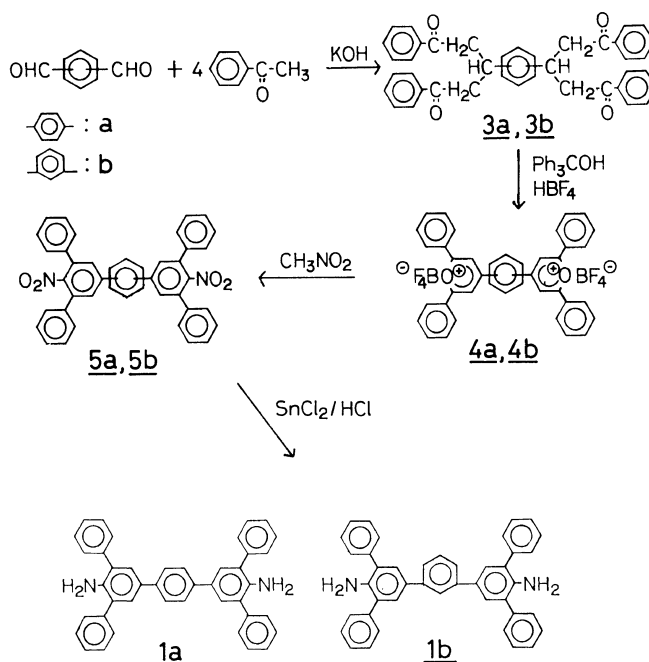
Inherent viscosities were measured at a concentration of 0.5 g dl^{-1} at 30°C . Infrared (IR) spectra were recorded on a Beckman FT2100 spectrometer with KBr disks. ^1H NMR spectra were recorded on a Varian T60 NMR spectrometer. Thermogravimetric analysis (TGA) was conducted with a DuPont Model 951 thermogravimetric analyzer at a heating rate of $10^\circ\text{C min}^{-1}$ in 100 ml min^{-1} of N_2 or air flow. Differential scanning calo-

rimetry (DSC) was performed on a DuPont 1090 thermal analyzer in combination with a DSC cell at a heating rate of $20^\circ\text{C min}^{-1}$ in 60 ml min^{-1} of N_2 flow. Wide angle X-ray scattering (WAXS) was conducted on a Rigaku X-ray diffractometer with nickel-filtered Cu-K_α radiation (38 kV, 30 mA) and a Laue camera. Solubility of the polymers was evaluated by mixing the polymers and solvents for 24 hours. Optical microscopic observation was carried out on a Nikon type 104 polarized-light transmission microscope.

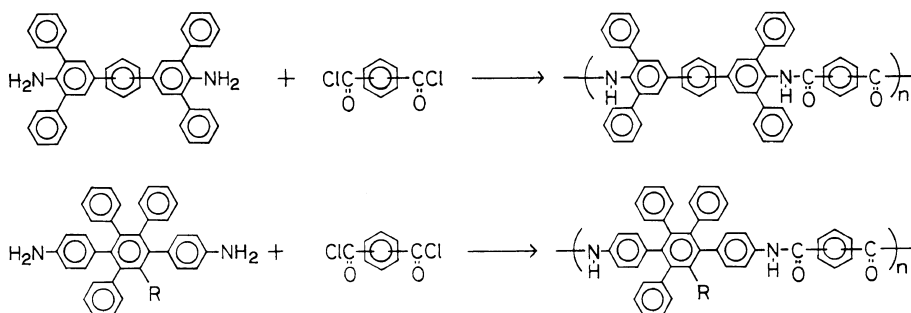
RESULTS AND DISCUSSION

Monomer Synthesis

New diamines containing two phenyl groups on the *o*-positions of amino groups were prepared as shown in Scheme 1. Terephthalaldehyde and isophthalaldehyde were reacted with acetophenone to yield the tetraketones (**3a**, **3b**). The bispyrylium salts (**4a**, **4b**) were derived from **3a** and **3b**, though relatively long reaction time (17 hours)



Scheme 1.



Scheme 3.

Table I. Synthesis of polyamides

Diamine	Diacid chloride	Condition		Outlook	Yield %	η_{inh}^a dl g ⁻¹	Film
		Concn.	Additive				
1a	TPC	5%	no	Turbid	89	0.83	no
	TPC	7%	Li ₂ CO ₃	Transparent	85	0.97	no
	IPC	7%	no	Transparent	93	0.47	yes
1b	TPC	8%	no	Transparent	99	0.62	yes
	IPC	13%	no	Transparent	89	0.28	no
2a	TPC	14%	no	Transparent	97	2.87	yes
	IPC	14%	no	Transparent	97	0.88	yes
2b	TPC	8%	no	Precipitate	78	0.46 ^b	no
	TPC	14%	LiCl	Cloudy	83	0.93 ^b	no
	IPC	14%	no	Precipitate	91	0.49 ^b	yes
	IPC	15%	LiCl	Cloudy	81	0.46 ^b	yes

^a Inherent viscosity measured at a concentration of 0.5 g dl⁻¹ in NMP at 30°C except for **b**.

^b NMP containing LiCl was used as a solvent.

chloride (IPC) was carried out by low-temperature solution condensation in NMP (Scheme 3). The results are summarized in Table I.

Precipitate of **1a**/TPC polyamide appeared during the polymerization in NMP. When polymerized in the presence of Li₂CO₃, the reaction mixture was a clear solution and gave the polymer with inherent viscosity of 0.97. However, the molecular weight was not high enough to form a film. Polymers, **1a**/IPC, **1b**/TPC, and **1b**/IPC was polymerized as a homogeneous solution. The polymers **1a**/IPC and **1b**/TPC gave flexible and tough films. Relatively low viscosities of these polymers may be attributed to the steric hindrance of

the diamines due to the bulky side groups on the *o*-position of the amino groups.

The polymerization using **2a** gave polyamides having good solubility and high viscosity to form tough films. The polymer made of **2a** and TPC gave the highest inherent viscosity of 2.87 in this series. In the case of **2b**, on the other hand, both polymers derived from TPC and IPC precipitated during the polymerization in NMP. The polymerization in the presence of LiCl did not improve the solubility remarkably, and did not increase the inherent viscosity so much

Table II. Characterization of polyamides

Polymer		η_{inh} dl g ⁻¹	T_g^a °C	TGA/°C ^b		Solubility ^c	
Diamine	Diacid chloride			N ₂	Air	NMP	CHCl ₃
1a	TPC	0.97	—	508	482	+	—
	IPC	0.47	299	482	485	++	—
1b	TPC	0.62	327	477	467	++	—
	IPC	0.28	275	466	567	++	—
2a	TPC	2.87	—	508	493	++	—
	IPC	0.88	349	509	520	++	—
2b	TPC	0.93	—	516	524	—	—
	IPC	0.49	—	514	516	—	—

^a T_g determined by DSC at a heating rate of 20°C min⁻¹ in N₂.

^b 5% weight-loss temperature on TGA at a heating rate of 10°C min⁻¹ in 100 ml min⁻¹ flow of N₂ or air.

^c ++, soluble; +, partially soluble; —, insoluble.

Characterization

Thermal transition behaviors were evaluated by DSC measurement. The polymers containing *m*-catenation showed the glass transitions at 275–349°C, except for **2b**/IPC polyamide (Table II). The polymers in which all linkages are *p*-catenated did not show clear glass transition. All the polymers did not show melting behavior below their decomposition temperatures, though X-ray diffraction measurement showed that the polymers had more or less semi-crystalline characteristics. The X-ray diffraction photograph of **2a**/TPC is shown in Figure 1 as an example.

All the polymers showed good thermal stability on the TGA measurements; 5 wt% weight-loss temperatures were in the range of 466–524°C. There was no remarkable difference in measuring atmosphere, N₂ or air.

The polymers derived from **1b** and **2a** showed good solubility in NMP. The flexible structure by *m*-catenation in the former and the interference of polymer chain packing by the unsymmetrical structure in the latter contributed to improve their solubilities. The diamines which have *p*-catenated and symmetrical structure (**1a** and **2b**) made the polymers less soluble in NMP. Monomer crystallinity of

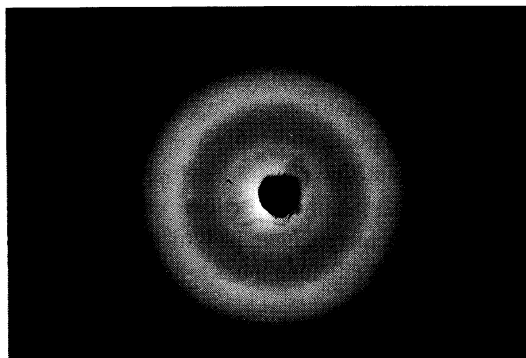


Figure 1. X-Ray diffraction photograph of the **2a**/TPC polyamide.

2b, which showed an extremely high melting temperature, may be responsible for the fact that the polymers derived from **2b** had the lowest solubility in this series.

In the three rigid-rod polyamides, **2a**/TPC polyamide showed the highest viscosity and the best solubility. Preliminary microscopic observation for **2a**/TPC polyamide solution in NMP was carried out at room temperature. A 20% solution was obtained from the polymerization solution directly, and observed through an optical microscope under cross polarization. Some part of the solution showed

Table III. Microscopic observation of **2a**/TPC polyamide solution in NMP containing LiCl under crossed polarization

Polymer concentration	Under shear	No shear
20%	Colorful birefringence	Partially colorful birefringence
17%	Colorful birefringence	Monochlomic birefringence
15%	Bright ↔ dark	Dark
10%	Slightly bright ↔ dark	Dark
5%	Dark	Dark

colorful birefringence and the other part showed monochlomic birefringence. In the case of a 20% NMP solution containing LiCl, some part showed colorful birefringence, and the other part showed color only under applied shear, and relaxed to an isotropic phase quickly. The relation of microscopic appearance and polymer concentration is listed in Table III. These anisotropic behaviors suggest that **2a**/TPC polyamide solution in NMP forms a liquid crystalline phase. Further evaluations, including the concentration effect on the absolute viscosity of the polymer solution, are involved in the future work.

REFERENCES

- M. Kakimoto, M. Yoneyama, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 149 (1988).
- S. S. Mohite, N. N. Maldar, and C. S. Marvel, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 2777 (1988).
- F. Akutsu, K. Matsuo, K. Naruchi, and M. Miura, *Polym. Commun.*, **30**, 182 (1989).
- Y. Oishi, S. Harada, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 3393 (1989).
- A. E. Lozano, J. G. de la Campa, and J. de Abajo, *Makromol. Chem., Rapid Commun.*, **11**, 471 (1990).
- Y. Oishi, H. Takado, M. Yoneyama, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 1763 (1990).
- J. Lin, Y. Yuki, H. Kunisada, and S. Kondo, *J. Appl. Polym. Sci.*, **40**, 2113 (1990).
- M. Xie, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **29**, 55 (1991).
- H. Jeong, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **29**, 767 (1991).
- G. Liou, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **29**, 995 (1991).
- J. Y. Jadhav, W. R. Krigbaum, and J. Preston, *Macromolecules*, **21**, 538 (1988).
- J. Y. Jadhav and W. R. Krigbaum, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 1175 (1989).
- W. Hatke, H. Schmidt, and W. Heitz, *J. Polym. Sci., Polym. Chem. Ed.*, **29**, 1387 (1991).
- W. Hatke, H. Land, H. Schmidt, and W. Heitz, *Makromol. Chem., Rapid Commun.*, **12**, 235 (1991).
- F. W. Harris and Y. Sakaguchi, *Proc. Polym. Mater. Sci. Eng.*, **60**, 187 (1989).
- S. V. Krivun and G. N. Dorofeenko, *Khim. Getero. Soedi.*, **2**, 656 (1966).
- W. Foerst, "Newer Method of Preparative Organic Chemistry," Vol. III, Academic Press, New York, 1964, p 415.
- H. Saikachi and Y. Taniguchi, *Yakugaku Zasshi*, **88**, 1054 (1968).
- E. C. Horning, Ed., "Org. Synth.," Coll. Vol. 3, John Wiley & Sons, New York, 1955, p 806.
- L. F. Fieser, "Organic Experiments," 2nd ed, Heath, D. C., Co., Lexington, MA, 1968, p 297.