Dyes and Pigments 26 (1994) 247-255

0143-7208/94/$7.00

ELSEVIER 0143-7208(94)00026-3

Synthesis and Fluorescence Properties of Substituted Pyrenylpyridine Derivatives

Jyh Jian Chen & Ing Jing Wang

Department of Textile Engineering, National Taiwan Institute of Technology,
Taipei, Taiwan

(Received 24 May 1994; accepted 4 July 1994)

ABSTRACT

A series of 3-substituted-1-pyrenylpropenone and 2-methyl-3-cyano-4-substituted-6-pyrenylpyridine derivatives were synthesized; IR, ^{1}H-NMR and mass spectra data of these compounds were measured, and their structure was confirmed by IR, ^{1}H-NMR and elemental analysis. The electronic absorption spectra and fluorescence behaviour of the 2-methyl-3-cyano-4-substituted-6-pyrenylpyridine derivatives were also studied.

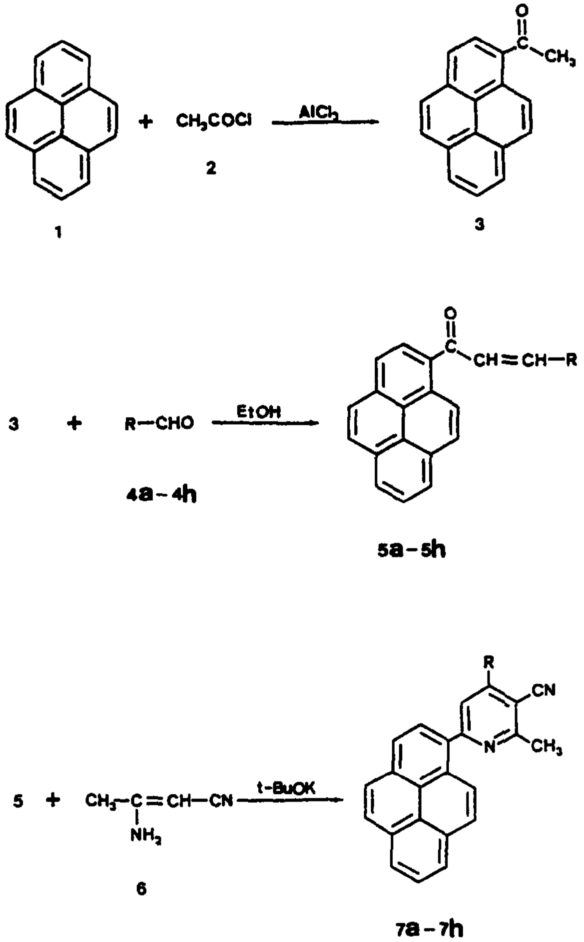
1 INTRODUCTION

Many structural types of aromatic and heteroaromatic systems can be used as components in fluorescent whitening agents or dyes, and find wide application in textile and paper industries. One of these structural classes comprises a pyrene moiety in combination with heteroaromatic systems, such as 2-phenyl-5-(1-pyrenyl)-1,3,4-oxadiazole[1] and 2,4-dimethoxy-6-(1-pyrenyl)-1,3,5-triazine.[2-3] These compounds act as fluorescent whitening agents suitable for polyester fabrics, but have only moderate fastness. We report here the preparation and properties of some derivatives of pyrenylpyridines; these compounds were synthesised using a modified synthetic method used for pyridine derivatives.[4-7]

2 RESULTS AND DISCUSSION

2.1 Preparation and structure determination

The reaction routes to the 2-methyl-3-cyano-4-substituted-6-pyrenylpyridines (**7a–7h**) are shown in Scheme 1. 3-Acetylpyrene (**3**) was prepared by the



Compound			R
4a	5a	7a	Phenyl
4b	5b	7b	4-(Dimethylamino)phenyl
4c	5c	7c	4-Cyanophenyl
4d	5d	7d	4-Methoxyphenyl
4e	5e	7e	1-Naphthyl
4f	5f	7f	2-Furyl
4g	5g	7g	2-Thienyl
4h	5h	7h	2-Pyridyl

Scheme 1

reaction of pyrene (**1**) with acetyl chloride (**2**) in the presence of aluminium chloride as catalyst,[8–12] and was then condensed with aromatic and heteroaromatic aldehydes (**4a–4h**) in an alkali/ethanol medium to give the 3-substituted-1-pyrenylpropenone (**5a–5h**).[11,13] The desired 2-methyl-3-cyano-4-substituted-6-pyrenylpyridine compounds (**7a–7h**) were subsequently obtained by cyclization of **5a–5h** with *β*-aminocrotonitrile (**6**) in the presence of potassium *t*-butoxide as catalyst at room temperature. The structure of the compounds was confirmed by elemental analysis and by IR and ^{1}H-NMR.

The IR spectra of 3-acetylpyrene (**3**) showed a characteristic absorption band at 1666 cm^{-1} due to the carbonyl group. The ^{1}H-NMR spectra data of compound **3** in $CDCl_3$ showed a singlet at $\delta = 2{\cdot}88$ ppm, attributed to the 3H of the methyl group; a 1H doublet at $\delta = 8{\cdot}33$–$8{\cdot}35$ ppm was attributed to the proton at the 2-position of the pyrene ring and the other pyrene protons showed as a multiplet (8H) at $\delta = 7{\cdot}92$–$8{\cdot}27$ ppm. According to Dean and Gumprecht,[14–15] the acetyl group is in the 3-position of the pyrene ring.

The IR spectra of the 3-substituted-1-pyrenylpropenones (**5a–5b**) showed well-defined bands at 1641–1691 cm^{-1} due to the carbonyl group; compound **5c** also showed typical cyano absorption at 2223 cm^{-1}. The ^{1}H-NMR spectra of compounds **5a–5h** in $CDCl_3$ showed two doublets at $\delta = 6{\cdot}62$–$7{\cdot}82$ ppm, attributed to the two protons of the —CH=CH— group. Compound **5b** showed a singlet at $\delta = 3{\cdot}0$ ppm, attributed to the six protons of the methyl group of the dimethylamino substituent. Compound **5d** showed a singlet at $\delta = 3{\cdot}81$ ppm, attributed to the three protons of the methoxy group in the phenyl ring. Characteristic data for compounds **5a–5h** are given in Table 1.

The IR spectra of 2-methyl-3-cyano-4-substituted-6-pyrenylpyridines (**7a–7h**) showed a sharp absorption band at 2216–2228 cm^{-1} corresponding to the cyano group in the pyridine ring. The ^{1}H-NMR spectra of compounds **7a–7h** in $CDCl_3$ showed a singlet at $\delta = 2{\cdot}97$–$3{\cdot}07$ ppm, attributed to 3H of the methyl group at the 2-position of the pyridine ring, and a singlet at $\delta = 7{\cdot}68$–$7{\cdot}88$ ppm attributed to 1H at the 5-position of the pyridine ring; spectra data of compounds **7a–7h** are listed in Tables 2–3.

2.2 Electron spectra

The electronic spectra of 4-aryl-6-pyrenylpyridines (**7a–7e**) and 4-heteroaryl-6-pyrenylpyridines (**7f–7h**) were measured in ethyl acetate solution and the absorption maxima and the fluorescence emission maxima are

TABLE 1

IR and ^{1}H-NMR Data for 3-Acetylpyrene (**3**) and 3-Substituted-1-Pyrenylpropenones (**5a–5h**)

Compound No.	*IR* *νKBr (cm^{-1})*	^{1}*H-NMR : δ (ppm)* *(CDCl$_3$)*	
3	1666 [—C=O]	2·88	[s, 3H, $COCH_3$ on phenyl]
		7·96–8·24	[m, 8H, pyrene]
		8·33–8·35	[d, 1H, H-2 on pyrene]
5a	1656 [—C=O]	7·38–7·65	[m, 7H, C_6H_5 and —CH=CH—]
		8·01–8·26	[m, 8H, pyrene]
		8·58–8·61	[d, 1H, H-2 on pyrene]
5b	1641 [—C=O]	3·00	[s, 6H, —$N(CH_3)_2$ on phenyl]
		6·62	[m, 6H, C_6H_4 and —CH=CH—]
		7·19–7·54	
		7·99–8·22	[m, 8H, pyrene]
		8·51–8·54	[d, 1H, H-2 on pyrene]
5c	1659 [—C=O]	7·50–7·66	[m, 6H, C_6H_4 and —CH=CH—]
	2223 [—C≡N]	8·00–8·26	[m, 8H, pyrene]
		8·63–8·67	[d, 1H, H-2 on pyrene]
5d	1662 [—C=O]	3·81	[s, 3H, OCH_3 on phenyl]
		6·86–6·91	[m, 6H, C_6H_4 and —CH=CH—]
		7·29–7·59	
		7·95–8·23	[m, 8H, pyrene]
		8·55–8·58	[d, 1H, H-2 on pyrene]
5e	1651 [—C=O]	7·48–7·92	[m, 8H, naphthalene and —CH=CH—]
		8·02–8·35	[m, 8H, pyrene]
		8·50–8·55	[d, 1H, H-2 on naphthalene]
		8·69–8·72	[d, 1H, H-2 on pyrene]
5f	1655 [—C=O]	6·47–6·49	[q, 1H, H-4 on furan]
		6·66–6·67	[d, 1H, H-3 on furan]
		7·51–7·52	[d, 1H, H-5 on furan]
		7·33–7·46	[dd, 2H, —CH=CH—]
		7·95–8·36	[m, 8H, pyrene]
		8·62–8·65	[d, 1H, H-2 on pyrene]
5g	1691 [—C=O]	7·03–7·06	[q, 1H, H-4 on thiene]
		7·22–7·78	[m, 4H, H-3 and H-5 on thiene and —CH=CH—]
		8·00–8·22	[m, 8H, pyrene]
		8·58–8·61	[d, 1H, H-2 on pyrene]
5h	1666 [—C=O]	7·24–7·28	[q, 1H, H-5 on pyridine]
		7·45–7·73	[m, 4H, H-3 and H-4 on pyridine and —CH=CH—]
		8·00–8·35	[m, 8H, pyrene]
		8·65–8·67	[d, 1H, H-2 on pyrene]
		8·70–8·73	[d, 1H, H-6 on pyridine]

TABLE 2
IR and ^{1}H-NMR Data for 2-Methyl-3-Cyano-4-Substituted-6-Pyrenyl Pyridines (**7a**–**7d**)

Compound No.	*IR νKBr (cm^{-1})*	*^{1}H-NMR : δ (ppm) (CDCl$_3$)*	
7a	2221 [—C≡N]	3·02	[s, 3H, CH_3 on pyridine]
		7·51–7·72	[m, 6H, C_6H_5 and H-5 on pyridine]
		8·00–8·27	[m, 8H, pyrene]
		8·40–8·43	[d, 1H, H-2 on pyrene]
7b	2217 [—C≡N]	2·98	[s, 3H, CH_3 on pyridine]
		3·03	[s, 6H, —$N(CH_3)_2$ on phenyl]
		7·65–7·68	[dd, 4H, C_6H_4]
		7·99–8·26	[m, 8H, pyrene]
		8·38–8·41	[d, 1H, H-2 on pyrene]
7c	2219 [—C≡N]	3·03	[s, 3H, CH_3 on pyridine]
	2228	7·68	[m, 3H, H-5 on pyridine]
		7·76–7·85	[dd, 4H, C_6H_4]
		8·01–8·27	[m, 8H, pyrene]
		8·37–8·40	[d, 1H, H-2 on pyrene]
7d	2221 [—C≡N]	3·00	[s, 3H, CH_3 on pyridine]
		3·86	[s, 3H, OCH_3 on phenyl]
		7·04–7·67	[dd, 4H, C_6H_4]
		7·68	[s, 1H, H-2 on pyridine]
		7·99–8·26	[m, 8H, pyrene]
		8·34–8·41	[d, 1H, H-2 on pyridine]

listed in Table 4. It was found that substituents such as the *N*,*N*-dimethylamino group in **7b**, and the methoxy group in **7d** in the phenyl moiety at the 4-position of the pyridine ring had little influence on the absorption maxima compared to that of compound **7a**. The absorption maxima of compounds **7a**–**7e** were in the general range 360–372 nm. Replacement of the phenyl ring in **7a** by a heteroaryl ring, as in **7f**, **7g** and **7h**, caused a bathochromic shift of 8–10 nm, the absorption maxima of **7f**–**7h** being in the range 368–370 nm. Fluorescence emission maxima of 4-aryl-6-pyrenylpyridines (**7a**, **7d** and **7e**) were in the range 440–446 nm and these compounds showed intense blue fluorescence in ethyl acetate solution. Compound **7c**, with a cyano group as substituent in the phenyl ring, showed a strong bluish-green fluorescence with fluorescence emission maxima at 476 nm. Compound **7b**, containing an *N*,*N*-dimethylamino group in the phenyl ring, had the largest fluorescence emission maxima at 520 nm, but showed a weak green fluorescence. The 4-heteroaryl-6-pyrenylpyridines (**7f**–**7h**) had fluorescence emission in the 453–460 nm range and showed greenish-blue fluorescence.

TABLE 3
IR and ^{1}H-NMR Data for 2-Methyl-3-Cyano-4-Substituted-6-Pyrenyl Pyridines (7e–7h)

Compound No.	*IR νKBr (cm^{-1})*	*^{1}H-NMR : δ (ppm) (CDCl$_3$)*	
7e	2220 [—C≡N]	3·07	[s, 3H, CH_3 on pyridine]
		7·53–7·62	[m, 6H, naphthalene]
		7·78	[s, 1H, H-5 on pyridine]
		7·99–8·24	[m, 9H, pyrene and H-2 on naphthalene]
		8·48–8·51	[d, 1H, H-2 on pyrene]
7f	2219 [—C≡N]	2·97	[s, 3H, CH_3 on pyridine]
		6·63–6·44	[q, 1H, H-4 on furan]
		7·61–7·62	[d, 1H, H-3 on furan]
		7·66–7·67	[d, 1H, H-5 on furan]
		8·00–8·27	[m, 8H, pyrene]
		8·36–8·39	[d, 1H, H-2 on pyrene]
7g	2217 [—C≡N]	2·99	[s, 3H, CH_3 on pyridine]
		7·22–7·23	[m, 1H, H-4 on thiene]
		7·53	[d, 1H, H-3 on thiene]
		7·54–7·55	[d, 1H, H-5 on thiene]
		7·78	[s, 1H, H-5 on pyridine]
		7·97–8·27	[m, 8H, pyrene]
		8·35–8·39	[d, 1H, H-2 pyrene]
7h	2216 [—C≡N]	3·04	[s, 3H, CH_3 on pyridine]
		7·40–7·44	[s, 2H, H-3' and H-5' on pyridine]
		7·88–7·91	[m, 2H, H-4' and H-5 on pyridine]
		7·99–8·26	[m, 8H, pyrene]
		8·39–8·42	[d, 1H, H-2 on pyrene]
		8·81–8·82	[d, 1H, H-6' on pyridine]

3 EXPERIMENTAL

All melting points are uncorrected. IR spectra were recovered on a JASCO Hc-2 FT-IR/IR-3 (KBr). ^{1}H-NMR spectra were determined with a JUM-FX-100 (JEOL) FT–NMR spectrometer using TMS as internal standard; mass spectra were determined on a JEOL JMS-D-300; absorption spectra on a Shimadzu UV-240 and fluorescence spectra on a Perkin-Elmer LS 50. The concentration of the ethyl acetate solution used for these measurements was 5×10^{-8} M.

3.1 3-Acetylpyrene (3)

Acetyl chloride (7·8 g, 0·1 mole) and aluminium trichloride (13·3 g, 0·1 mole) were added to dichloromethane (200 ml), and the mixture was

TABLE 4
Absorption and Fluorescence Spectra Data for 2-Methyl-3-Cyano-4-Substituted-6-Pyrenylpyridines (**7a–7h**) in Ethyl Acetate

Compound No.	λ_{max} *(nm)*	*Log ε*	λ_{em} *(nm)*
7a	360	4·40	446
7b	365	4·63	520
7c	372	4·43	476
7d	360	4·52	440
7e	362	4·52	443
7f	370	4·43	453
7g	369	4·52	453
7h	368	4·45	460

cooled to below 5°C. The mixture was stirred vigorously and pyrene (20·2 g, 0·1 mole) in dichloromethane (70 ml) was slowly added over 1 h. The resulting solution was stirred at 20°C for 3–4 h and the mixture then poured into 800 g ice–water. The organic layer was dried ($MgSO_4$), solvent removed and the resultant oil crystallized from ethanol to give greenish-yellow crystals (75%), m.p. 67–70°C (P^+ at m/e 244). Calculated for $C_{18}H_{12}O$: C, 88·52; H, 4·92. Found: C, 88·10; H, 50·1.

3.2 Compounds 5a–5h

To prepare 3-phenyl-1-pyrenylpropenone (**5a**), a mixture of 3-acetylpyrene (4·88 g, 0·2 mole), benzaldehyde (2·12 g, 0·02 mole), ethanol (50 ml) and sodium hydroxide (0·6 g, 0·015 mole) was stirred at room temperature overnight. During the reaction, a yellow product precipitated. The crude product was filtered and recrystallized from ethanol to give yellow crystals (71%), m.p. 96–98°C (P+ at m/e 332). Calculated for $C_{25}H_{16}O$: C, 90·36; H, 4·82. Found: C, 89·81; H, 5·34.

Similarly prepared were compounds **5b–5h**:

3-(4-Dimethylaminophenyl)-1-pyrenylpropenone (**5b**) was recrystallized from ethanol as orange crystals (90%), m.p. 170–173°C (P^+ at m/e 375). Calculated for $C_{27}H_{21}NO$: C, 86·40; H, 5·60; N, 3·70. Found: C, 86·16; H, 5·62; N, 3·41.

3-(4-Cyanophenyl)-1-pyrenylpropenone (**5c**) was recrystallized from ethanol as yellow crystals (70%), m.p. 175–180°C (P^+ at m/e 357). Calculated for $C_{26}H_{15}NO$: C, 87·39; H, 4·20; N, 3·92. Found: C, 86·72; H, 4·58; N, 3·58.

3-(4-Methoxyphenyl)-1-pyrenylpropenone (**5d**) was recrystallized from ethanol as yellow crystals (65%), m.p. 120–125°C (P^+ at m/e 362). Calculated for $C_{26}H_{18}O_2$: C, 86·18; H, 4·97. Found: C, 85·83; H, 5·12.

3-(1-Naphthyl)-1-pyrenylpropenone (**5e**) was recrystallized from ethanol as yellow crystals (90%), m.p. 119–120°C (P^+ at m/e 382). Calculated for $C_{29}H_{18}O$: C, 91·09; H, 4·71. Found: C, 90·89; H, 4·88.

3-(2-Furyl)-1-pyrenylpropenone (**5f**) was recrystallized from ethanol as yellow crystals (83%), m.p. 144–146°C (P^+ at m/e 322). Calculated for $C_{23}H_{14}O_2$: C, 85·71; H, 4·34. Found: C, 85·19; H, 4·48.

3-(2-Thienyl)-1-pyrenylpropenone (**5g**) was recrystallized from ethanol as yellow crystals (88%), m.p. 155–157°C (P^+ at m/e 338). Calculated for $C_{23}H_{14}OS$: C, 81·65; H, 4·14, Found: C, 81·63: H, 4·41.

3-(2-Pyridyl)-1-pyrenylpropenone (**5h**) was recrystallized from ethanol as yellow crystals (60%), m.p. 72–75°C (P^+ at m/e 333). Calculated for $C_{24}H_{15}NO$. C, 86·48; H, 4·50; N, 4·20. Found: C, 85·80; H, 4·89; N, 4·06.

3.3 Compounds 7a–7h

To prepare 2-methyl-3-cyano-4-phenyl-6-pyrenylpyridine (**7a**), a mixture of 3-phenyl-1-pyrenylpropenone (**5a**; 1 g, 0·003 mole), β-aminocrotonitrile (2·5 g, 0·03 mole) and potassium *t*-butoxide (0·6 g) in acetonitrile (50 ml) was stirred at room temperature overnight. The resultant precipitate was filtered, dried and recrystallized from acetone to give yellow–green crystals (65%), m.p. 178–179°C (P^+ at m/e 394). Calculated for $C_{29}H_{18}N_2$: C, 88·32; H, 4·56; N, 7·10. Found: C, 87·81; H, 4·88; N, 7·05.

Compounds **7b**–**7h** were similarly prepared:

2-Methyl-3-cyano-4-(4-dimethylaminophenyl)-6-pyrenylpyridine (**7b**) was recrystallized from acetone as yellow–green crystals (80%), m.p. 221–229°C (P^+ at m/e 437). Calculated for $C_{31}H_{23}N_3$: C, 85·12; H, 5·26; N, 9·61. Found: C, 84·81; H, 5·24; N, 9·22.

2-Methyl-3-cyano-4-(4-cyanophenyl)-6-pyrenylpyridine (**7c**) was recrystallized from acetone as yellow crystals (71%), m.p. 220–223°C (P^+ at m/e 419). Calculated for $C_{30}H_{17}N_3$: C, 85·91; H, 4·05; N, 10·02. Found: C, 85·45; H, 4·20; N, 9·89.

2-Methyl-3-cyano-4-(4-methoxyphenyl)-6-pyrenylpyridine (**7d**) was recrystallized from acetone as yellow–green crystals (61%), m.p. 168–171°C (P^+ at m/e 424). Calculated for $C_{30}H_{20}N_2O$: C, 84·90; H, 4·71; N, 6·60. Found: C, 84·21; H, 4·97; N, 6·39.

2-Methyl-3-cyano-4-(1-naphthylphenyl)-6-pyrenylpyridine (**7e**) was recrystallized from acetone as yellow–green crystals (60%), m.p. 204–210°C (P^+ at m/e 444). Calculated for $C_{33}H_{20}N_2$: C, 89·18; H, 4·50; N, 6·31. Found: C, 88·64; H, 4·84; N, 6·44.

2-Methyl-3-cyano-4-(2-furyl)-6-pyrenylpyridine (**7f**) was recrystallized from acetone as yellow–green crystals (81%), m.p. 207–210°C (P^+ at m/e 384). Calculated for $C_{27}H_{16}N_2O$: C, 84·37; H, 4·16; N, 7·29. Found: C, 84·10; H, 4·28; N, 7·00.

2-Methyl-3-cyano-4-(2-thienyl)-6-pyrenylpyridine (**7g**) was recrystallized from acetone as yellow–green crystals (77%), m.p. 206–210°C (P^+ at m/e 400). Calculated for $C_{27}H_{16}N_2S$: C, 81·00; H, 4·00; N, 7·00. Found: C, 80·41; H, 4·19; N, 6·84.

2-Methyl-3-cyano-4-(2-pyridyl)-6-pyrenylpyridine (**7h**) was recrystallized from acetone as yellow–green crystals (59%), m.p. 224–228°C (P^+ at m/e 395). Calculated for $C_{28}H_{17}N_3$: C, 85·06: H, 4·30; N, 10·63. Found: C, 84·55; H, 4·59; N, 10·32.

REFERENCES

1. Atkinson, J. R., Br. Pat. Appl. 122970; *Chem. Abstr.*, **74** (1971) 127557.
2. Imperial Chemical Industries Ltd., French Pat. Appl. 1556896; *Chem. Abstr.*, **72** (1970) 45036.
3. Luethi, C., Ger. Pat. Appl. 2232729; *Chem. Abstr.* **78** (1973) 125845.
4. Shibata, K., Urano, K. & Matsui, M., *Bull. Chem. Soc. Jpn*, **61** (1988) 2199.
5. Shibata, K., Katasuyma, I., Matsui, M. & Muramatsu, H., *Bull. Chem. Soc. Jpn*, **63** (1990) 3710.
6. Shibata, K., Katasuyma, I., Matsui, M. & Muramatsu, H., *J. Heterocyclic Chem.*, **28** (1991) 161.
7. Matsui, M., Matsumoto, K., Shibata, K. & Muramatsu, H., *Dyes and Pigments*, **18** (1992) 47.
8. Freeman, H. S. & Posey, J. C., Jr, *Dyes and Pigments*, **18** (1992) 171.
9. Tietze, L.-F. & Eicher, T., *Reaktionen and Synthesen im Organish-chemischen Praktium*. Georg Thieme Verlag Stuttgat, New York, 1964, p. 127.
10. Gore, P. H., in *Friedel-Crafts and Related Reaction*, ed. G. A. Olah. Interscience, New York, 1964.
11. *Vogel's Textbook of Practical Organic Chemistry*, Fourth edn. Jwang Yuan Pub., New York, 1978, p. 770.
12. McCrae, W., *Basic Organic Reaction*. Heyden & Son Ltd., New York, 1984, p. 58.
13. Adams, R., Johnson, J. R. & Wilcox, C. F., *Laboratory Experiments in Organic Chemistry*. Macmillan Pub., New York, 1981, p. 354.
14. Dean, J. A., *Handbook of Organic Chemistry*. McGraw-Hill, New York, 1987, pp. 1–7.
15. Gumprecht, W. H., *Org. Syntheses Coll.*, Vol. **5** (1973).