Benzoin Condensation Reactions of 5-Membered Heterocyclic Compounds

Chang Kiu Lee*

Department of Chemistry, Kangweon National University,
Chuncheon 200-701, Korea

Mi Soon Kim, Jin Soon Gong and In-Sook Han Lee

Department of Science Education, Kangweon National University,
Chuncheon 200-701, Korea

Received August 23, 1991

Benzoin condensation reactions of 2-thiophenecarboxaldehydes and furfurals have been reexamined with catalysts such as potassium cyanide, cyanide-resin, and a thiazolium salt. 2-Thiophenecarboxaldehydes gave both thenoins and thenils while furfurals gave only furoins. Possible routes which might lead to formation of thenils were investigated.

J. Heterocyclic Chem., **29**, 149 (1992).

Aldehydes of heterocyclic aromatic compounds are commonly used as substrates of benzoin condensation reaction. Furfural (**1c**) is the most frequently used one among them. Presence of the hetero atom does not seem to cause any difference in reaction mechanism although the yields may vary depending on the catalysts. For example, the yield of furoin (**2c**) from **1c** was 38% when potassium cyanide was used, which is in strong contrast to 92% yield of benzoin from benzaldehyde [1]. The yield of thenoin (**2a**) from 2-thiophenecarboxaldehyde (**1a**) under the similar reaction conditions was 30% [2] or 32% [3]. The yield of thenoin (**2a**) seemed to be much higher than 30% in one report [4], since the yield of thenil which was hypothetically the product of the oxidation of thenoin (the yield of thenoin was not given) was 64%. However, some of the thenil may have formed independently.

On the other hand, pyrroloin (**2e**) did not form from 2-pyrrolecarboxaldehyde (**1e**) [5] or its 3-isomer [6]. The yield of **2c** was remarkably increased (88%) when an *N*-benzylthiazolium salt was used as a catalyst [7]. No report of the preparation of **2a** using a thiazolium salt catalyst has appeared in the literature.

In the course of our research in synthesis of imidazolinones from condensation reactions of urea with α-hy-

Table I

Benzoin Condensation Reactions of 1

Reagent (mole)	Ethanol (ml)	Water (ml)	Catalyst/Additive	Time hour	Product (% yield) [a]
1a (0.05)	15	10	[b]	1.5	**1a** [c] (50), **2a** (0.5), **3a** (0.4)
1a (0.05)	15	10	[b]/oxygen	2	**1a** [c] (45), **2a** (0.5), **3a** (0.5)
1a (0.05)	15	10	[b]/nitrogen	2	**1a** [c] (45), **2a** (0.7), **3a** (0.5)
1a (0.05)	50	0	[d]/nitrogen	2	**1a** [c] (40), **2a** (10), **3a** (12)
1a (0.05)	50	15	[d]/nitrogen	2	**1a** [c] (30), [e]
1a (0.05)	10 [f]	0	thiazolium salt	2	**2a** (20), **3a** (55)
1b (0.02)	4	3	[b]	2	**2b** (10), **3b** (20), [e]
1b (0.06)	60	5	[b]/nitrogen	1	**1b** [c] (50), **2b** (4), **3b** (7)
1b (0.01)	10	0	[d]/nitrogen	1	**1b** [c] (60), **2b** (10), **3b** (15)
1b (0.05)	10 [f]	0	thaizolium salt	2	**2b** (10), **3b** (16)
1c (0.15)	15	10	[b]	1.5	**2c** (21)
1c (0.15)	15	10	[b]/nitrogen	1.5	**2c** (30)
1c (0.15)	50	15	[d]/nitrogen	1.5	**2c** (12)
1c (0.15)	50	0	[d]	2	**2c** (40)
1c (0.15)	10 [f]	0	thaizolium salt	2	**2c** (90)
1d (0.15)	15	10	[b]/nitrogen	1.5	**2d** (20)
1d (0.15)	50	15	[d]/nitrogen	1.5	**2d** (50)
1d (0.15)	10 [f]	0	thaizolium salt	2	**2d** (90)
4 (0.02)	15	10	[b]/nitrogen	1.5	**5** (10)
4 (0.03)	15	0	[d]/nitrogen	1.5	**5** (30)
4 (0.03)	10 [d]	0	thaizolium salt	2	**5** (64)

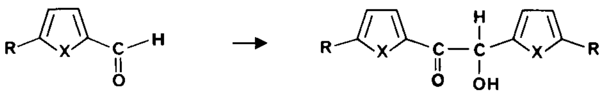
[a] Isolated yield, [b] Potassium cyanide. [c] Recovery. [d] Cyanide-resin. [e] Unidentifiable gum. [f] Trieylamine was also added; ethanol:triethylamine = 2:1 by volume.

droxyketone compounds we came to prepare furoins and thenoins from furfurals and thiophenecarboxaldehydes, respectively. Although the preparation of furoin (**2c**) followed the observation reported in the literature, we could hardly reproduce the results in regard to thenoin (**2a**). The most unusual observation was the formation of thenil (**3a**) beside **2a** when **1a** was treated with various catalysts. We report the results of our extensive reexamination of the benzoin condensation reaction of 5-membered heterocyclic aromatic aldehydes.

Results and Discussion.

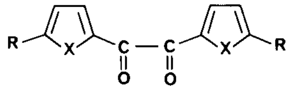
We were puzzled at first by the extremely low yield of thenoin (**2a**, *ca.* 0.5%) and the formation of thenil (**3a**, *ca.* 0.5%) from the reaction of **1a** and potassium cyanide as the catalyst in ethanol-water. Although commercial potassium cyanide was used without purification **1a** and ethanol were distilled prior to use. The only difference in the conditions of the present reaction compared to the method in the literature was the smaller scale of the reaction (0.01-0.05 mole *vs.* 0.1-0.3 mole of **1a** [2,4]). More than 50% of **1a** was recovered after workup (see Experimental) and both **2a** and **3a** were isolated regardless of the reaction time or the compositions of the solvents (Table I). The percent recovery of **1a** after the reaction was calculated from the absorbance in the ultraviolet spectra and also from the intensity of the bands in the gas chromatograms, in addition to the isolation by column chromatography, or by direct distillation of the reaction mixture. In all cases with potassium cyanide 50-80% of unreacted **1a** was present.

Formation of thenil (**3a**) was observed even when a different catalyst such as 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium bromide was used. We prepared a new catalyst, namely cyanide-resin, by stirring Dowex 1X8-100 with potassium cyanide solution, and employed it for benzoin condensations. With this catalyst **2a** and **3a** formed in *ca.* 10% and 12% yield, respectively. Therefore, formation of **3a** during the benzoin condensation reaction of **1a** seemed to be taking place regardless of the catalysts.



2

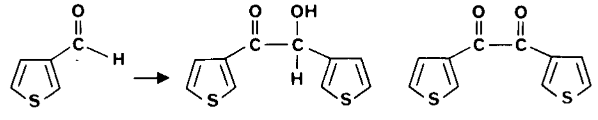
	X	R
1a	S	H
b	S	CH_3
c	O	H
d	O	CH_3
e	NH	H



3

Furfural (**1c**), on the other hand, gave only furoin (**2c**) under similar reaction conditions in which **2a** and **3a** were isolated. The yield of **2c** was low, 20-30%, when potassium cyanide was used. The highest yield (40%) was obtained when cyanide-resin was used. The catalytic activity of the cyanide-resin did not decrease after three runs. Although the yield with cyanide-resin is far lower in one than that with the thiazolium salt (90%) the experimental procedure seems to be convenient and the cost affordable. When the thiazolium salt was used the yields of thenoin (**2a**) and thenil (**3a**) was 20% and 55%, respectively. Furthermore, **3a** was precipitated out first from the reaction mixture. Similarly, **3b** was isolated from the reactions of **1b** as the major product in addition to **2b**.

In contrast to the formation of both **2a** and **3a** only 3,3′-thenoin (**5**) was isolated from the reaction of 3-thiophenecarboxaldehyde (**4**) in 64% yield. 3,3′-Thenil (**6**) did not form under any reaction conditions employed with **1a** and **1b**. Several attempts to prepare pyrroloin (**2e**) with different catalysts under various reaction conditions were all unsuccessful.



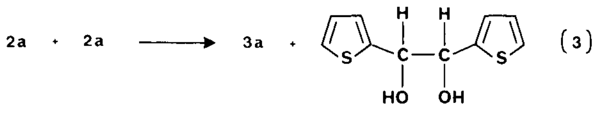
4 5 6

The formation of thenil (**3a**) may be rationalized by four possible routes as shown in Equations 1-4: (1) oxidation of thenoin during the reaction by air; (2) thermal dehydrogenation; (3) self-oxidation-reduction of thenoin (**2a**) to **3a** and 1,2-di-2-thienyl-1,2-ethanediol (**7**); and (4) oxidation-reduction reaction of **1a** and **2a** leading to **3a** and 2-thienylmethanol (**8**).

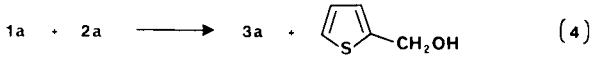
Oxidation reactions of α-hydroxyketones to α-diketones are well known reaction which can be easily achieved by various oxidizing agents. Conversion of **2c** to **3c**, in particular, has been widely investigated using metal ions such as copper [8-12], antimony [13,14], nickel [15], cerium [16,17], or iron [18]. Oxides of bismuth [19] or manganese [20] or thalium ethoxide [21] were also used. The Oppenauer oxidation reaction of **2c** to **3c** with triphenoxyaluminum and acetone [22] or benzophenone [23] were reported. Oxidation by blowing air in the presence of cupric acetate [24], bismuth oxide [25] or by saturated oxygen [26] are known.

$$2a \xrightarrow{O_2} 3a \qquad (1)$$

$$2a \xrightarrow{heat} 3a \qquad (2)$$



7



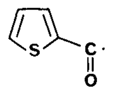
8

However, there has been no report of conversion of **2a** to **3a** by air. Iodine was used for such conversion [2]. We examined extensively the effect of bubbling oxygen or nitrogen gas during the reaction, but the yield of **3a** did not change noticeably. Therefore, we ruled out the possibility of oxidation by air (Equation 1).

The second possibility (Equation 2) was considered at first because **2a** seemed to convert into **3a** when **2a** was examined by gas chromatography. Approximately one-third of the **2a** was changed to **3a** as it passed through the column (see Experimental). Similar conversions were observed with **2c** (60%) or benzoin (42%). About 60% of benzoin was converted into benzil by heating 0.1 g of the sample at 220° for 1 hour. The conversion was very efficient with **2a**, being completed in 10 minutes when 0.1 g of the sample was heated in the open air at 220°. Conversion of furoin (**2c**) into furil (**3c**) was rather slow, being about 10% completed under the similar conditions. Dehydrogenation of **2a** at high temperature (220°) is not surprising; however, a similar reaction did not take place when **2a** (neat or in ethanol solution) was heated at 80° for several hours. Therefore, thermal dehydrogenation could be ruled out at this stage.

The most likely pathway may be either Equation 3 or Equation 4. They represent disproportionation of **2a** or hydrogen transfer from **2a** to **1a**. If the 2-thienylglycol (**7**) is present in the reaction mixture one may conclude that the reaction follows Equation 3. On the other hand, presence of 2-thienylmethanol (**8**) after the reaction should support the route shown in Equation 4. However, a series of efforts to detect either **7** or **8** in the reaction mixture gave negative result. First, **7** was prepared by reducing **2a** with sodium borohydride in ethanol and the pure compound was used as the standard for thin layer chromatography (R_f 0.35, silica gel, chloroform-methanol 9:1; 0.51, 4:1) and gas chromatography.

Based on our observation we came to realize that the formation of **3a** during the benzoin condensation of **1a** may be the result of different reaction pathway. Although we have not a definite evidence we suggest a radical reaction may be taking place in view of the formation of a deep green color during the reaction and the feasibility of stabilization of the radical such as A by the sulfur atom.



A

EXPERIMENTAL

Melting points were determined on a Fisher Mel-Temp apparatus and are uncorrected. Infrared (ir) spectra were recorded on a Perkin-Elmer Model 1430 spectrophotometer, and the ultraviolet-visible spectra were recorded on a Hitachi U-3200 double-beam spectrophotometer. Nuclear magnetic resonance (nmr) spectra were recorded on a Varian EM-390 spectrometer and a Bruker 300 MHz FT-nmr spectrometer with TMS as internal standard. Electron impact mass spectra (ms) were obtained by Kratos MS 25 RFA spectrometer. Elemental analyses were performed by the Korea Basic Research Center, Seoul. Gas chromatograms were obtained using a Varian Vista 6000 gas chromatograph equipped with a capillary column (DB-1701, 0.25 mm I.D., 30 m) and a flame ionization detector (conditions: initial temperature 150°; initial hold 2 minutes; temperature increase 6°/minute; final temperature 300°).

Starting Materials.

Compounds **1a-e**, **4** and **8** were commercial products from the Aldrich Chemical Co., which were distilled under vacuums prior to use. Thenils **3a,b** and furils **3c,d** were prepared for use as standards by oxidation of thenoins **2a,b** and furoins **2c,d**, respectively, by following the methods in the literatures [2].

Preparation of Cyanide-resin.

A mixture of Dowex 1 x 8-100 (10 g) and 20% aqueous solution of potassium cyanide (100 ml) was gently stirred for 24 hours. The mixture was filtered and the resin was washed 3-4 times with distilled water. The resin was left for 10-15 minutes on the Buchner funnel which was connected to suction flask so that maximum amount of water was sucked out and then used immediately.

Preparation of 3-Benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium Bromide.

A solution of 5-(2-hydroxyethyl)-4-methyl-1,3-thiazole (5.13 g, 35.8 mmoles) and benzyl bromide (6.16 g, 36.0 mmoles) in ether (20 ml) was heated at reflux for 4.5 hours. The solution was cooled to room temperature and then kept in a refrigerator overnight to give a solid mass. The solid was crushed and washed with ether and then recrystallized from absolute ethanol, 7.36 g (67%), mp 109-110°, ir (potassium bromide): 3380 s (OH), 3035 m, 2950 w, 2910 w, 2875 w, 1590 m, 1460 s, 1410 w, 1360 w, 1172 w, 1062 m, 1060 m, 745 m, 705 m cm^{-1}; ^{1}H nmr (deuterium oxide): δ 2.52 (s, 3 H, CH_3), 3.18 (t, 2 H, $=C-CH_2$, J = 6.50 Hz), 3.90 (t, 2 H, CH_2O, J = 6.50 Hz), 4.78 (s, 1 H, OH), 5.73 (s, 2 H, $CH_2C_6H_5$), 7.45 (m, 5 H, C_6H_5), 9.28 (s, 1 H, 2-H).

Anal. Calcd. for $C_{13}H_{16}BrNOS$: C, 49.69; H, 5.13; Br, 25.43; N, 4.46; S, 10.20. Found: C, 49.44; H, 5.00; Br, 25.71; N, 4.27; S, 10.15.

General Procedure for Benzoin Condensation Reactions.

With Potassium Cyanide.

To an ethanol (10 ml) solution of the aldehyde **1** (0.05 mole) was added potassium cyanide (5-10 mmoles) in water (5 ml). The mixture turned to deep green within a minute. It was heated at reflux for predetermined period of time (Table I). After cooling, the solution was left in a refrigerator for 1-2 days. In some instances the solution was neutralized with acetic acid to *p*H 5-6 and then left in a refrigerator for 1-2 days. In case of the thiophenes **1a,b** no precipitate formed; but the furoins **2c,d** usually precipitated which were collected by filteration (10-20% yield). The reaction mixture of **1a** or **1b** was poured into water (50 ml) and then extracted with chloroform (3 x 30 ml). The organic extract was dried over sodium sulfate and then the solvent was removed to dryness. The residual viscous liquid was redissolved into abs. ethanol (*ca.* 5 ml) and decolorized once with charcoal. Upon cooling in a refrigerator the thenils **3a,b** usually precipitated first. In many cases the mixture was chromatographed on a column of silica gel eluting with benzene to separate the thenils **3** first and then with benzene-chloroform (9:1) to isolate the thenoins **2**.

With Cyanide-resin.

A mixture of **1** (0.05 mole) and cyanide-resin (5 g) in ethanol (50 ml) was heated at reflux for 1-3 hours. The hot mixture was filtered to remove the resin and the filtrate was evaporated under vacuum to reduce the volume to *ca.* 10 ml. Upon cooling in a refrigerator the thenils **3a** and **3b** or the furoins **2c** and **2d** precipitated. The solid was collected by filteration and dried. The filtrate was chromatographed on a column of silica gel for further separation of other components (Table I).

With the Thiazolium Salt.

The procedure is essentially similar to the one in the literature [7]. However, **2** and **3** were separated by column chromatography if no precipitate formed after workup.

5,5'-Dimethylthenoin (**2b**).

This compound had mp 88-90°; ir (potassium bromide): 3360 m (OH), 3080 vw, 2910 w, 1645 s (C=O), 1448 s, 1382 m, 1270 s, 1242 m, 1200 m, 1160 ms, 1046 s, 915 ms, 802 s, cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.41 (s, 3H, 5'-CH$_3$), 2.51 (s, 3 H, 5-CH$_3$), 4.29 (d, 1 H, OH, J = 6.42 Hz), 5.86 (d, 1 H, C*H*OH, J = 6.42 Hz), 6.59 (d, 1 H, 4'-H, J = 3.50 Hz), 6.76 (d, 1 H, 3'-H, J = 3.50 Hz), 6.95 (d, 1 H, 4-H, J = 3.75 Hz, 7.57 (d, 1 H, 3-H, J = 3.75 Hz); ^{13}C nmr (deuteriochloroform): ppm 15.34, 15.96, 71.50, 125.18, 126.84, 127.13, 134.91, 137.03, 139.92, 141.48, 151.60, 189.48; ms: m/e (%) 254 (3, M$^+$ +2), 252 (13, M$^+$), 235 (53, M$^+$ -OH), 207 (12), 155 (6), 128 (17), 127 (76, CH$_3$-C$_4$H$_2$S-CHOH), 126 (11), 125 (54, CH$_3$-C$_4$H$_2$S-CO), 99 (16), 88 (56), 86 (92), 84 (100).

Anal. Calcd. for C$_{12}$H$_{12}$O$_2$S$_2$: C, 57.11; H, 4.79; S, 25.41. Found: C, 57.23; H, 4.95; S, 25.28.

5,5'-Dimethylfuroin (**2d**).

This compound had mp 91.5-93°; ir (potassium bromide): 3500 s (OH), 3095 w, 2910 w, 1645 s, 1620 s, 1575 w, 1488 w, 1440 w, 1383 w, 1362 w, 1276 m, 1205 s, 1186 w, 1042 w, 1022 s, 990 w, 975 w, 821 w, 780 m cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.19 (s, 3 H, 5'-CH$_3$), 2.32 (s, 3 H, 5-CH$_3$), 4.00 (broad s, 1 H, OH, J = 6.42 Hz), 5.61 (s, 1 H, C*H*OH), 5.86 (d, 1 H, 4'-H, J = 3.49 Hz), 6.10 (d, 1 H, 3'-H, J = 3.49 Hz), 6.20 (d, 1 H, 4-H, J = 3.68 Hz), 7.08 (d, 1 H, 3-H, J = 3.68 Hz); ^{13}C nmr (deuteriochloroform): ppm 13.40, 13.93, 68.94, 106.65, 109.35, 109.86, 122.10, 126.56, 148.83, 152.91, 159.19, 183.58; ms: m/e (%) 220 (39, M$^+$), 203 (88, M$^+$ -OH), 175 (20), 112 (31), 111 (100, CH$_3$-C$_4$H$_2$O-CHOH), 110 (28), 109 (88, CH$_3$-C$_4$H$_2$O-CO), 88 (26), 86 (89).

Anal. Calcd. for C$_{12}$H$_{12}$O$_4$: C, 65.45; H, 5.49. Found: C, 65.72; H, 5.33.

5,5'-Dimethylthenil (**3b**).

This compound had mp 83-84°; ir (potassium bromide): 3080 vw, 3055 vw, 2910 vw, 2842 vw, 1632 vs, 1510 w, 1420 vs, 1375 m, 1330 s, 1220 s, 1182 m, 1160 m, 1032 m, 815 s, 800 s, 770 w, 730 w cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.55 (s, 6 H, 5- and 5'-CH$_3$), 6.83 (d, 2 H, 4- and 4'-H, J = 4.05 Hz), 7.81 (d, 2 H, J = 4.05 Hz); ^{13}C nmr (deuteriochloroform): ppm 16.09, 127.53, 136.63, 137.85, 153.80, 182.37; ms: m/e (%) 252 (2, M$^+$ +2), 250 (18, M$^+$), 126 (21), 125 (100, CH$_3$-C$_4$H$_2$S-CO), 97 (16), 86 (18), 84 (27).

Anal. Calcd. for C$_{12}$H$_{10}$O$_2$S$_2$: C, 57.57; H, 4.03; S, 25.62. Found: C, 57.44; H, 3.82; S, 25.87.

5,5'-Dimethylfuril (**3d**).

This compound had mp 161-162°; ir (potassium bromide): 3110 m, 2925 vw, 1630 vs, 1503 s, 1455 vw, 1382 w, 1290 w, 1211 m, 1046 m, 1032 ms, 950 w, 846 vw, 828 w, 810 w, 752 ms cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.43 (s, 6 H, 5- and 5'-CH$_3$), 6.22 (d, 2 H, 4- and 4'-H, J = 4.05 Hz), 7.50 (d, 2 H, J = 4.05 Hz); ^{13}C nmr (deuteriochloroform): ppm 14.21, 110.10, 126.64, 138.60, 161.19, 176.72; ms: m/e (%) 218 (42, M$^+$), 111 (35), 109 (100, CH$_3$C$_4$H$_2$O-CO), 88 (30), 86 (87), 84 (92), 53 (78), 52 (21).

Anal. Calcd. for C$_{12}$H$_{10}$O$_4$: C, 66.05; H, 4.62. Found: C, 66.33; H, 4.78.

Preparation of 1,2-Di-2-thienyl-1,2-ethanediol (**7**).

To a cooled (0°) solution of **2a** (0.41 g, 1.8 mmoles) in 95% ethanol (20 ml) was added sodium borohydride (0.07 g, 1.8 mmoles). The mixture was gradually brought to room temperature and stirred until the starting material was not detected by thin layer chromatography (*ca.* 2 hours). The solution was evaporated to dryness, resulting a colorless gum. Water (20 ml) was added and the solution was extracted with ether using a continuous extractor for 20 hours. The ethereal was dried over sodium sulfate and evaporated to dryness to give a colorless gummy solid which was recrystallized from ethanol-ether, 0.30 g (72%), mp 90° (lit. [2] 90-91°).

Examination of Acyloins with Gas Chromatography.

One μl of each solutions of the acyloins (1 x 10^{-1} *M*) was injected and the area point of the peak corresponding to the benziltype compound was compared to that of the pure benzils of known concentration. The retention time (minutes) and the percent conversion of acyloins to acyloils are: benzoin (11.59) - benzil (11.39), 42%; **2a** (14.98) - **3a** (14.51), 35%; **2b** (19.12) - **3b** (18.91), 60%; **2c** (9.03) - **3c** (7.82), 60%; **2d** (14.21) - **3d** (13.89), 20%.

Acknowledgments.

We thank professor Maurice M. Kreevoy of University of Minnesota for helpful discussion and proof of the manuscript. We also thank the Korea Science and Engineering Foundation for financial support (891-0302-017-1).

REFERENCES AND NOTES

[1] W. S. Ide and J. S. Buck, *Org. React.*, **4**, 269 (1949).

[2] I. Deschamps, W. J. King and F. F. Nord, *J. Org. Chem.*, **14**, 184 (1949).

[3] S. Z. Cardon and H. P. Lankelma, *J. Am. Chem. Soc.*, **70**, 4248 (1948).

[4] R. D. Schuetz and G. P. Nilles, *J. Org. Chem.*, **36**, 2486 (1971).

[5a] W. Herz and J. Brasch, *J. Org. Chem.*, **23**, 1513 (1958); [b] T. S. Gardner, E. Wenis and J. Lee, *J. Org. Chem.*, **23**, 823 (1958).

[6] H. J. Anderson and H. Nagy, *Can. J. Chem.*, **59**, 1961 (1972).

[7] H. Stetter, R. Y. Ramsch and H. Kuhlmann, *Synthesis*, 733 (1976).

[8] Y. Matsui, T. Yokoi and K. Mochida, *Chem Letters*, 1037 (1976).

[9] V. M. S. Ramanujam, S. Sundaran and N. Venkatasabramanian, *Indian J. Chem.*, **9**, 1015 (1971).

[10] M. Weise and M. Appel, *J. Am. Chem. Soc.*, **70**, 3666 (1948).

[11] H. Firouzabadi, A. R. Sardarian, M. Naderi and B. Vessal, *Tetrahedron*, **40**, 5001 (1984).

[12] K. Mochida, T. Nakamura and Y. Matsui, *Shimane daigaku Nogakubu Kenkyu Hokoku*, 156 (1983); *Chem. Abstr.*, **102**, 203450u (1985).

[13] J. Yamamoto, Y. Tanioka and M. Umezu, *Bull. Chem. Soc. Japan*, **55**, 3035 (1982).

[14] J. Yamamoto, M. Murakami, N. Kameoka, N. Otami, M. Umezu and T. Matsuura, *Bull. Chem. Soc. Japan*, **55**, 345 (1982).

[15] S. Mineo and K. Nakagawa, *Yakugaku Zasshi*, **94**, 1180 (1974).

[16] T.-L. Ho, *Synthesis*, 560 (1972).

[17] H. Firouzabadi, N. Iranpoor, H. Parham and J. Tootan, *Synth. Commun.*, **14**, 631 (1984).

[18] R. A. El Zaru and A. A. Jarrar, *Chem. Ind. (London)*, 741 (1977).

[19] W. Rigby, *J. Chem. Soc.*, 793 (1951).

[20] L. Turner, *J. Am. Chem. Soc.*, **76**, 5175 (1954).

[21] L. P. Mehatton and M. J. Soulal, *J. Chem. Soc.*, 4095 (1953).

[22] R. N. Gupta and S. S. Deshapande, *Agra Univ. J. Res.*, **7**, 103 (1958); *Chem. Abstr.*, **53**, 17053g (1959).

[23] J. Stanek and J. Zemlieka, *Chem. Listy*, **51**, 493 (1957); *Chem. Abstr.*, **51**, 10048h (1957).

[24] J. G. M. Bremner and D. G. Jones and Imperial Chemical Industries Ltd., British Patent 605,021 (1948); *Chem. Abstr.*, **43**, 690f (1949).

[25] B. Holden and W. Rigby, *J. Chem. Soc.*, 1924 (1951).

[26] S. Shinkai, T. Kunitake and T. C. Burice, *J. Am. Chem. Soc.*, **96**, 7140 (1974).