Studies on Isoxazoles. XI. Pyrolyses of 4-Isoxazolin-3-thiones\(^9\)

SOJI SUGAI and KAZUO TOMITA

Agricultural Chemicals Research Laboratories, Sankyo Co., Ltd.\(^9\)

(Received June 14, 1979)

Novel pyrolysis reactions of 4-isoxazolin-3-thiones (X) are described, affording two regioisomeric 1,4-dithiins (III, IV) and thioacetamides (XI). Among the thioacetamides, N-methylbenzoylthioacetamide (XIIe) was identical with an authentic sample prepared by the reduction of 2-methyl-5-phenyl-4-isoxazolin-3-thione (Xe) with thiophenol. The structures of the dithiins were deduced from the physicochemical data, especially the shielding and deshielding effects in the NMR spectra. A mechanism for the reactions is proposed by analogy with the thermal isomerization of 3-isoxazolones into 2-oxazolones. In order to account for the formation of the isomeric dithiins, a thiirene intermediate (II) was assumed to be involved in the reaction pathway.

**Keywords**—pyrolysis of 4-isoxazolin-3-thiones; thermal ring transformations; 1,4-dithiins; thioacetamides; thiirene intermediates; shielding and deshielding effects; sulfur radicals

In the previous paper,\(^4\) it was reported that 3-alkylthio-2-benzylisoxazolium halides afforded 3-alkylthioisoxazoles on heating, with elimination of benzyl halides. Pyrolysis of the corresponding 2-ethyl derivatives, however, gave unexpected results, which are discussed in detail in the present paper.

Treatment of 3-ethoxy carbonylmethylthio-2-ethyl-5-methylisoxazolium bromide (I) (Chart 1) in boiling toluene gave fine yellow needles in poor yield. The structure was deduced from the physicochemical data. The results of elemental analysis and the molecular peak \((M^+, m/e 286)\) indicated the formula \(C_{12}H_{18}N_2O_2S_2\). The nuclear magnetic resonance (NMR) spectrum showed a triplet \((3H, J=7 \text{~Hz})\) at \(\delta 1.28\), a singlet \((6.5H)\) at \(\delta 2.33\), a singlet \((2.5H)\) at \(\delta 2.43\), a quintet-like peak \((2H)\) at \(\delta 3.53\) and a broadband peak \((1H)\) at \(\delta 10.83\), as shown in Fig. 1. On addition of deuterium oxide, the broad peak disappeared and the quintet turned into a quartet \((J=7 \text{~Hz})\); this was ascribed to an ethylaminogroup \((\text{NHCH}_2\text{CH}_3)\). The extraordinarily low chemical shift of \(\text{NH}\) suggested an intramolecular hydrogen bond\(^5\) with a hetero atom, which was assumed to be a carbonyl oxygen. In fact, a carbonyl group conjugated with strong electron releasing functions\(^6\) was indicated by \(\nu_{\text{C}=\text{O}}: 1580 \text{~cm}^{-1}\) in the infrared (IR) spectrum. Fragment peaks in mass spectrum (MS) are shown in Fig. 2, where two peaks at \(m/e 243\) \((M^+-43)\) and \(m/e 43\) indicate an acetyl group. Another peak \((m/e 143)\) suggested a symmetrical structure for \(M^+ (m/e 286)\), in which two pairs of an acetyl \((\text{C}_2\text{H}_4\text{O})\) and an ethylamino group \((\text{C}_2\text{H}_5\text{N})\) might be included. Extrusion of one pair \((\text{C}_2\text{H}_5\text{NO})\) from the half-S molecule \((\text{C}_5\text{H}_9\text{NS})\) leaves a \(\text{C}_2\text{S}\) group, which could be assigned to a thiirene ring \((-\hat{C}=-\hat{C}-)\). Thus, a 2-acetyl-3-ethylaminothiirene (II\(\text{b}\)) structure was assumed for the half molecule. The dimerization of II\(\text{b}\) could give two regioisomers, 2,6-diacyct-3,5-bis(ethylamino)-1,4-dithiin (III\(\text{b}\)) and 2,5-diacyct-3,6-bis(ethylamino)-1,4-dithiin (IV\(\text{b}\)). Therefore, the two methyl peaks

2) A part of this work was presented at the 11th Congress of Heterocyclic Chemistry, Kanazawa, October 1978.
at δ 2.43 and δ 2.33 in the NMR spectrum (Fig. 1) were ascribed to the two kinds of acetyl groups in IIIb and IVb. On the other hand, 2,3-bis(trifluoromethyl)-1,4-dithiin (V) has been synthesized by the thermal reaction of an acetylene (VI) with 3,4-bis(trifluoromethyl)-1,2-dithieterne (VII). This reaction assisted the interpretation of two fragment peaks, which were tentatively assigned to an acetylene (VIII, m/e 111) and a dithieterne (IX, m/e 175). This supports the proposed structures (IIIb, IVb) shown in Chart 1.

It has been reported\(^7\) that 2-benzyl-3-ethoxycarbonylmethylthio-5-phenylisoxazolium bromide was converted to 2-benzyl-5-phenyl-4-isoxazolin-3-thione in boiling acetonitrile, with elimination of ethyl bromoacetate. In the transformation of I into \(1,4\)-dithiins (IIib, IVb), therefore, 2-ethyl-5-methyl-4-isoxazolin-3-thione (Xb) derived from I could be involved as an intermediate (Chart 1). Because of the absence of aromaticity, the N–O bond of isoxazolines readily undergoes homolysis.\(^7\) It thus seems reasonable to consider that homolytic cleavage of the N–O bond in Xb initiates the reaction, resulting in the formation of \(1,4\)-dithiins (IIib, IVb). Therefore, a series of 4-isoxazolin-3-thiones (X)\(^8\) was pyrolyzed in boiling toluene. From each reaction (Xa—c, Table I), a mixture of the corresponding \(1,4\)-dithiins (IIia—c, IVa—c) was obtained (Chart 2). Two singlets assigned to the acetyl groups were observed (Table I) in the NMR spectrum of each reaction mixture. Among these peaks, only a singlet at \(\delta 2.17\) in the mixture of IIic and IVc appeared at relatively high field compared with the other singlets; this can be attributed to a shielding effect of a benzene ring. In order to confirm this, the conformations of the two isomers (IIic, IVc) were examined as shown in Chart 2. The methyl group in IVc could be distant from the benzene ring on the same side of the dithiin ring because of the hydrogen bond. However, it would be located over the benzene ring on the opposite side in a boat conformation of the dithiin ring.\(^9\) Therefore, the methyl signals at \(\delta 2.17\) and \(\delta 2.47\) could be ascribed to the acetyl group in IVc and in IIic, respectively. The two \(1,4\)-dithiins (IIic, IVc) were separated by several recrystallizations (Table I). There was no difference in the other spectral data (IR, ultraviolet (UV), MS) of IIic and IVc. Comparing the chemical shifts of the methyl groups \(\left(R^3\right)\) in IIic and IVc with those in the products from Xa and Xb, the isolated major

\[
\text{R}^1\text{O} \xrightarrow{\Delta} \begin{array}{c} \text{R}^1 \text{O} \\ \text{R}^2 \text{N} \text{R}^2 \end{array} \]

\[
\begin{array}{c}
\text{III} \\
\text{IV} \\
\text{XI}
\end{array}
\]

\[
\begin{array}{c}
\text{IIIa} : \text{R}^1 = \text{Me} \\
\text{IIIc} : \text{R}^1 = \text{Ph}
\end{array}
\]

\[
\begin{array}{c}
\text{IVa} : \text{R}^1 = \text{Me} \\
\text{IVc} : \text{R}^1 = \text{Ph}
\end{array}
\]

\[
\begin{array}{c}
\text{IVc} : \text{R}^1 = \text{Ph}
\end{array}
\]

\[
\text{XI}^\prime
\]

\[
\text{R}^1\text{O} \xrightarrow{\Delta} \begin{array}{c} \text{R}^1 \text{O} \\ \text{R}^2 \text{N} \text{R}^2 \end{array} \]

\[
\begin{array}{c}
\text{III} \\
\text{IV} \\
\text{XI}
\end{array}
\]

\[
\begin{array}{c}
\text{IIIa} : \text{R}^1 = \text{Me} \\
\text{IIIc} : \text{R}^1 = \text{Ph}
\end{array}
\]

\[
\begin{array}{c}
\text{IVa} : \text{R}^1 = \text{Me} \\
\text{IVc} : \text{R}^1 = \text{Ph}
\end{array}
\]

\[
\text{XI}^\prime
\]

\[
\begin{array}{c}
\text{R}^1\text{O} \xrightarrow{\Delta} \begin{array}{c} \text{R}^1 \text{O} \\ \text{R}^2 \text{N} \text{R}^2 \end{array} \]

\[
\begin{array}{c}
\text{III} \\
\text{IV} \\
\text{XI}
\end{array}
\]

\[
\begin{array}{c}
\text{IIIa} : \text{R}^1 = \text{Me} \\
\text{IIIc} : \text{R}^1 = \text{Ph}
\end{array}
\]

\[
\begin{array}{c}
\text{IVa} : \text{R}^1 = \text{Me} \\
\text{IVc} : \text{R}^1 = \text{Ph}
\end{array}
\]

\[
\text{XI}^\prime
\]


isomers could be assigned as IIIa and IIIb, and the minor isomers as IVa and IVb, respectively.

The reaction\(^8\) of 3-chloro-5-methyl-2-phenylisoxazolium chloride with sodium hydro-
sulfide gave a single 1,4-dithiin (III\(\text{d}\)) instead of 5-methyl-2-phenyl-4-isoxazolin-3-thione (X\(\text{d}\)), which might be too labile to permit its isolation. The structure of III\(\text{d}\) was deduced from the chemical shifts of its acetyl groups, which were compatible with those in the corresponding 1,4-dithiins (III\(\text{a}–\text{c}\)) (Table I).

### Table I. Pyrolyses\(^6\) of 4-Isoxazolin-3-thiones (X)

<table>
<thead>
<tr>
<th>X (\begin{array}{c} R^1 \ R^2 \end{array})</th>
<th>Yield %</th>
<th>NMR (CDCl(_3)) (\delta)</th>
<th>IR (Nujol) (\nu \text{ cm}^{-1})</th>
<th>UV (EtOH) (\lambda_{\text{max}} \text{ nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(R^1)</td>
<td>(R^2)</td>
<td>NH</td>
</tr>
<tr>
<td>a Me Me</td>
<td>20.8</td>
<td>Me</td>
<td>2.42 (s)</td>
<td>3.17 (d) (^f)</td>
</tr>
<tr>
<td>b Me Et</td>
<td>27.6</td>
<td>Me</td>
<td>2.43 (s)</td>
<td>3.53 (q) (^g)</td>
</tr>
<tr>
<td>c Me CH(_2)Ph</td>
<td>20.0</td>
<td>Me</td>
<td>2.47 (s)</td>
<td>4.37 (d) (^g)</td>
</tr>
<tr>
<td>d(^b) Me Ph</td>
<td>5.0</td>
<td>Me</td>
<td>2.53 (s)</td>
<td>6.80—7.20 (m)</td>
</tr>
<tr>
<td>e Ph Me</td>
<td>9.0</td>
<td>Ph</td>
<td>7.17—7.50 (m)</td>
<td>3.11 (d) (^f)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>IV(^e)</th>
<th>Yield %</th>
<th>NMR (CDCl(_3)) (\delta)</th>
<th>XI Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(R^1)</td>
<td>(R^2)</td>
</tr>
<tr>
<td>a (0.8) (^g)</td>
<td>Me</td>
<td>2.33 (s)</td>
<td>3.21 (d) (^f)</td>
</tr>
<tr>
<td>b (3.5) (^g)</td>
<td>Me</td>
<td>2.33 (s)</td>
<td>3.53 (q) (^g)</td>
</tr>
<tr>
<td>c 5.3</td>
<td>Me</td>
<td>2.17 (s)</td>
<td>4.80 (d) (^g)</td>
</tr>
<tr>
<td>d(^b)</td>
<td>0</td>
<td>Ph</td>
<td>7.10—7.46 (m)</td>
</tr>
<tr>
<td>e 4.6</td>
<td>Me</td>
<td>7.10—7.46 (m)</td>
<td>3.26 (d) (^f)</td>
</tr>
</tbody>
</table>

\(^a\) All reactions except for that of X\(\text{d}\) were carried out at 100—110\(^\circ\)C for 3 hr in toluene.

\(^b\) The reaction was carried out at 100—110\(^\circ\)C for 4 hr in CHCl\(_3\).

\(^c\) The yields were calculated from the NMR spectral data.

\(^d\) IVc: IR \(\nu_{\text{max}} \text{ cm}^{-1}: 3150, 1580\). UV \(\lambda_{\text{max}} \text{ nm}: 224, 244\. IVc: IR \(\nu_{\text{max}} \text{ cm}^{-1}: 3130, 1585\).

\(^e\) A quartet-like peak.

\(^f\) \(J=8 \text{ Hz}\).

\(^g\) \(J=6 \text{ Hz}\).

\(^h\) \(J=7 \text{ Hz}\).
On the pyrolysis of 2-methyl-5-phenyl-4-isoxazolin-3-thione (Xe),\textsuperscript{81} two 1,4-dithiins were obtained. The chemical shifts of the N-methyl groups in the major isomer were equivalent to those in IIIa (Table I). This suggested that the isomer was IIIe, as shown in Chart 2. In minor isomer, which was tentatively assigned as 1Ve, the N-methyl groups were assumed to be located near the benzene rings coplanar with the conjugated cline functions; the methyl signal was, therefore, shifted downfield by a deshielding effect.

Thioacetamides (XIa—e) were also obtained from the reactions of Xa—e (Chart 2, Table I). The thioacetamides in solution were in equilibrium with the corresponding enols (XI'), which were detected by means of the hydroxyl and vinlylic proton peaks in the NMR spectra. Among them, a stable N-methylbenzyloxythioacetamide (XIe) was shown to be identical with an authentic sample unambiguously prepared by mild reduction of Xe with thiophenol.

**Table II.** Physical Data for 1,4-Dithiins (III, IV) and Thioacetamides (XI)

<table>
<thead>
<tr>
<th>mp</th>
<th>Formula</th>
<th>Analyses (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C; H; N; S</td>
<td>C; H; N; S</td>
</tr>
<tr>
<td>IIIa</td>
<td>195—196</td>
<td>C_{10}H_{14}N_{2}O_{2}S_{2}</td>
</tr>
<tr>
<td>IIIb</td>
<td>164—166</td>
<td>C_{12}H_{18}N_{2}O_{3}S_{2}</td>
</tr>
<tr>
<td>IIIc</td>
<td>182—183</td>
<td>C_{22}H_{32}N_{2}O_{5}S_{2}</td>
</tr>
<tr>
<td>IIId</td>
<td>166—168</td>
<td>C_{20}H_{19}N_{2}O_{2}S_{2}</td>
</tr>
<tr>
<td>IIIe</td>
<td>196—198</td>
<td>C_{18}H_{19}N_{2}O_{2}S_{2}</td>
</tr>
<tr>
<td>IVc</td>
<td>182—183</td>
<td>C_{22}H_{32}N_{2}O_{5}S_{2}</td>
</tr>
<tr>
<td>I Ve</td>
<td>190—192</td>
<td>C_{22}H_{32}N_{2}O_{5}S_{2}</td>
</tr>
<tr>
<td>XIa</td>
<td>Oil</td>
<td>C_{6}H_{12}NOS</td>
</tr>
<tr>
<td>XIb</td>
<td>Oil</td>
<td>C_{6}H_{12}NOS</td>
</tr>
<tr>
<td>XIc</td>
<td>43—44</td>
<td>C_{12}H_{18}NOS</td>
</tr>
<tr>
<td>XI d</td>
<td>70—73</td>
<td>C_{14}H_{16}NOS</td>
</tr>
<tr>
<td>XI e</td>
<td>120—122</td>
<td>C_{12}H_{11}NOS</td>
</tr>
</tbody>
</table>

Thermal transformations of Isoxazoles into oxazoles are well known,\textsuperscript{10} but no isomerizations into other heterocycles are known. Compounds similar to Xd, 2-phenyl-4-isoxazolin-3-ones (XII, R²=phenyl), were reported to be thermally converted to 3-phenyl-4-oxazolin-2-ones (XV, R²=phenyl)\textsuperscript{11} (Chart 3). A kinetic study of this reaction suggested that resonance-stabilized diradicals (XIII) might be involved in the first step. They cyclized into \alpha-lactams (XIV), then four-center rearrangements would lead to the final products (XV).

By comparison with the pathway of XII to XV, a mechanism for the reactions of X to III, IV and XI can be proposed as shown in Chart 3. The N=O bond of X undergoes homolysis to afford a C,N-diradical (XVI) similar to XIII. This rapidly isomerizes to a C,S-diradical (XVII), and then to another diradical (XVIII) via a thirene (II). From the radicals (XVII, XVIII) in equilibrium, two competitive reactions affording III and IV are presumed to proceed. Under the reaction conditions used, the intermediate radicals (XVI, XVII) would be terminated to give XI. Thiirenes similar to II have been considered as intermediates in photolysis and thermolysis reactions of 1,2,3-thiadiazoles\textsuperscript{12} and 1,2,3-benzothiadiazoles.\textsuperscript{13}

It is interesting that there is such a major difference between the products of the thermal reactions of 4-isoxazolin-3-thiones (X) and 4-isoxazolin-3-ones (XII). This can be interpreted in terms of differences in the stabilities of sulfur and oxygen radicals.

Experimental

All melting points are uncorrected. IR spectra were recorded on a Hitachi G3 spectrometer, UV spectra on a Beckmann DB spectrophotometer and MS spectra on a JEOL JMS-01SG mass spectrometer. NMR spectra were taken on Hitachi-Perkin Elmer R-24 (60 MHz) and Varian A-60 spectrometers using tetramethysilane as an internal standard. The abbreviations used are as follows: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad). Preparative thin-layer chromatography (TLC) was carried out on Merck TLC plates, Silica Gel 60F254 (layer thickness 2 mm), and spots were visualized by ultraviolet irradiation or by exposure to iodine. Columns for chromatography were prepared with Wakogel C-200 (100—200 mesh) (Wako Pure Chemical Co.).

Pyrolysis of 3-Ethoxyacetylthio-2-ethyl-5-methylisoxazolium Bromide (II).—A suspension of 1 (2.2 g) in toluene (20 ml) was heated at 110° for 1 hr. The solvent was evaporated off, and the residue was
purified by column chromatography (n-hexane-acetone = 30:1) to give a mixture of 2,6-diisocetyl-3,5-bis-(ethylamino)-1,4-dithiin (IIIb) and 2,5-diisocetyl-3,6-bis(ethylamino)-1,4-dithiin (IVb) (5:1 by NMR) (0.15 g, 7.4%), mp 155—157°. Anal. Calcd. for C₃₃H₇₅NₓO₁₅S₁₅: C, 50.32; H, 6.33; N, 9.78; S, 22.39. Found: C, 50.20; H, 6.27; N, 9.91; S, 22.74. IR ν_max cm⁻¹: 3120 (NH), 1580 (CO). The NMR peaks are shown in Fig. 1, and the mass fragment peaks in Fig. 2.

**Pyrolysis of 4-Isoxazolin-3-thiones (Xa—c,c)⁹**—General Procedure: A solution of Xa—c or e in toluene was heated at 100—110° for 3 hr. The solvent was evaporated off, and the residue was separated by column chromatography followed by preparative TLC to give the corresponding thioacetamides (Xia—c,e) and a mixture of 1,4-dithiins (IIIA—c,c, IVa—c,e). The contents of the 1,4-dithiins (IVa,b) were calculated from the NMR spectra of the mixtures. Pure 1,4-dithiins (IIIA—c,c, IVc,e) were obtained by several recrystallizations from acetone. The spectral data are listed in Table I, and the physical constants and the elemental analyses in Table II. N-Methylacetothioacetamide (Xia); NMR (CDCl₃) δ: 1.98 (0.45H, s, CH₃ of XIA), 2.31 (2.55H, s, CH₃ of XIA), 3.25 (3H, d, J = 7.5 Hz, NHCH₂ of XIA and XIA'), 4.03 (1.7H, s, CH₂ of XIA), 5.39 (0.15H, s, =CH— of XIA), 9.27 (1H, br, NH of XIA and XIA'), 13.97 (0.15H, s, OH of XIA'). IR ν_max cm⁻¹: 3280 (NH), 1715 (CO). MS m/e: 131 (M⁺), 88 (M⁺—COCH₃). N-Ethylthioacetothioacetamide (XIB); NMR (CDCl₃) δ: 1.30 (3H, t, J = 7.5 Hz, CH₂CH₂ of XIB and XIB'), 2.28 (0.3H, s, COCH₃ of XIB), 2.31 (2.7H, s, COCH₃ of XIB), 3.72 (2H, a quintet-like peak, CH₂CH₂ of XIB and XIB'), 3.98 (1.8H, s, COCH₃ of XIB), 5.32 (0.1H, s, =CH— of XIB), 9.12 (1H, br, NH of XIB and XIB'), 13.97 (0.1H, s, OH of XIB'). IR ν_max cm⁻¹: 3200 (NH), 1715 (CO). N-Benzylacetothioacetamide (XIC); NMR (CDCl₃) δ: 1.98 (0.6H, s, CH₃ of XIC), 2.21 (2.4H, s, CH₂ of XIC), 3.93 (1.6H, s, COCH₃ of XIC), 4.82 (2H, d, J = 5 Hz, NHCH₂ of XIC and XIC'), 5.49 (0.2H, s, =CH— of XIC), 9.20 (1H, br, NH of XIC and XIC'), 13.97 (0.2H, s, OH of XIC'). IR ν_max cm⁻¹: 3280 (NH), 1710 (CO). MS m/e: 207 (M⁺), 104 (M⁺—COCH₃). N-Methylbenzoylthioacetamide (XIE); NMR (CDCl₃) δ: 3.10 (0.45H, d, J = 5 Hz, CH₃ of XIE), 3.19 (2.55H, d, J = 5 Hz, CH₃ of XIE), 4.47 (1.7H, s, CH₃ of XIE), 6.06 (0.15H, s, =CH— of XIE), 7.2—8.2 (5H, m, C₆H₅ of XIE and XIE'), 9.30 (1H, br, NH of XIE and XIE'), 14.41 (0.15H, s, OH of XIE'). IR ν_max cm⁻¹: 3320 (NH), 1675 (CO). MS m/e: 193 (M⁺), 105 (C₆H₅CO⁻), 88 (M⁺—COCH₃).

**Reaction of 3-Chloro-5-methyl-2-phenylisoxazoloxal Chloride²⁹** with NaSH—An aq. solution (30 ml) of 3-chloro-5-methyl-2-phenylisoxazoloxal chloride (5.34 g) was treated with NaSH (2.73 g) under ice-cooling. The mixture was stirred at room temperature for 1 hr then extracted with CHCl₃ (20 ml x 3). The extract was allowed to stand at 10° for 48 hr. After removal of the solvent, the residue was separated by column chromatography (n-hexane-acetone = 30:1) to give 2,6-diisocetyl-3,5-dianilino-1,4-dithiin (IIId) (0.22 g, 5.0%) and N-phenylacetothioacetamide (XII) (1.16 g, 25.8%). The physical data are listed in Table I and Table II. XII: NMR (CDCl₃) δ: 1.97 (1.2H, s, CH₂ of XIId), 2.30 (1.8H, s, CH₃ of XIId), 4.07 (1.2H, s, CH₂ of XIId), 5.50 (0.4H, s, =CH— of XIId), 7.1—7.9 (5H, m, C₆H₅ of XIId and XIId'), 8.30 (0.4H, br, NH of XIId'), 10.75 (0.6H, br, NH of XIId), 14.33 (0.4H, s, OH of XIId). IR ν_max cm⁻¹: 3310 (NH), 1625 (CO). MS m/e: 193 (M⁺), 150 (M⁺—COCH₃).

**N-Methylbenzoylthioacetamide (XIE)**—A mixture of 2-methyl-5-phenyl-4-isoxazolin-3-thione (Xe) (1.0 g), thiophenol (1.15 g) and triethylamine (3 drops) in toluene (12 ml) was stirred at room temperature for 48 hr. After removal of the solvent, the crude product was purified by column chromatography (n-hexane-acetone = 10:1) to give Xe (0.82 g, 81.2%), mp 125—124°. The compound was identical (by NMR and IR spectra) with that obtained by the pyrolysis of Xe.

**Acknowledgement** We are grateful to Dr. S. Takahashi, the director, and Dr. M. Ishida, the vice director of our laboratories, for their encouragement throughout this work. We also thank Dr. M. Yoshimoto, Central Research Laboratories of Sankyo Co., Ltd. for valuable discussions.