A NOVEL APPROACH TO FUNCTIONALIZATION OF AZINES. OXIRANYL AND THIIRANYL DERIVATIVES OF PYRIDINE, QUINOLINE AND ISOQUINOLINE

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Abstract - Convenient methods for synthesis of the oxiranyl and thiiranyl derivatives of pyridine, quinoline and isoquinoline have been elaborated. Oxiranes have been synthesized from corresponding aldehydes with dimethylsulfonium methyldide in anhydrous medium. Exchange of the oxygen atom in the oxirane ring on sulfur with potassium thiocyanate gave thiiranylnazines.

Oxiranyl derivatives of aromatic compounds (oxiranylenenes) and their sulphur analogues (thiiranylenenes) could be used as substrates for preparation of many aromatic compounds bearing various substituents. Usefulness of oxiranylenenes in organic synthesis has been extensively reviewed and is of current interest.¹ The chemistry of thiiranylenenes is less developed, nevertheless some reactions useful in synthesis have been reported.² Oxiranylnazines remained generally unknown. Only oxiranylpyridines were mentioned in the literature³,⁴ but, except for 4-oxiranylpyridine,⁴ no spectroscopic and other physicochemical data have been reported. They have been reported as very unstable and reactive liquids. Thiiranylnazines remained still unknown.

The aim of our work was to elaborate the general methods for synthesis of oxiranyl and thiiranylnazines as the substrates useful in syntheses of the azoaromatic compounds substituted in the side chains.

The main step of the synthesis presented in this paper involves conversion of aldehydes ¹ into oxiranes ². Oxiranes thus obtained were easily converted into thiiranes ³ with are in some cases accompanied by vinyl derivatives ⁴.

\[
\begin{align*}
\text{Az-CHO} & \xrightarrow{\text{(CH\textsubscript{2})\textsubscript{2}S=CH\textsubscript{2}}} \text{Az} & \xrightarrow{\text{KSCN}} & \text{Az} \\
\text{C\textsubscript{6}H\textsubscript{6}, NaOH, TEBA} & & \text{C\textsubscript{2}H\textsubscript{5}OH, H\textsubscript{2}O} & \text{Az} & + & \text{Az}
\end{align*}
\]

 Az = pyridyl ¹αι–γ ₂αι–ζ ₂β–ζ ₄α–ζ
 Az = quinolyl ₁δ–ι ₂δ–ι ₃α–ι ₄δ–ι
 Az = isoquinolyl ₁κ,λ ₂κ,λ ₃κ,λ ₄κ,λ

Initially, we attempted to synthesize some oxiranylnazines by the method of Corey and Chaykowsky⁵ but the yields of desired products were low or the method did not work at all. The best results were achieved when the reaction was carried out with dimethylsulfonium methyldide generated in situ from trimethylsulfonium chloride in dry benzene with powdered NaOH in the presence of catalytical amounts of
TEBA according to the procedure elaborated recently in our laboratory for the synthesis of unstable oxiranylquinones. The products were isolated without partitioning between water and organic solvent, thus the deleterious effect of water was eliminated. When oxiranes were synthesized, the reaction was more effective with dimethyloxosulfonium methyldide as a reagent. Oxirane treated with methyl iodide (acetone, room temp., 24 h) gave methiodides except when steric hindrance of the electron pair of the nitrogen atom by the oxirane ring occurred or when they easily underwent decomposition. In these cases picrates were prepared. The results of the synthesis of oxiranylazines and their characteristics as well as melting points of their derivatives are listed in Table 1, and their H NMR spectra are given in Table 3.

For the synthesis of thiiranylazines, potassium thiocyanate was used as a reagent. It must be mentioned that stability of thiiranes was very low and some of them were accompanied by vinylazines as products of their thermal decomposition and in the cases of and only vinylazines were isolated. Nevertheless, as shown in Table 2, most thiiranyl derivatives of azines, being under investigation, can be synthesized in the satisfactory yield. H NMR data of thiiranylazines and vinylquinolines are given in Table 4.

Starting aldehydes were prepared by oxidation of methylazines with SeO₂. For the synthesis of 5- and 7-formylquinolines, the mixture of corresponding methylquinolines (synthesized from m-toluidine by the Skraup reaction using As₂O₅ as an oxidant) was oxidized with SeO₂ and aldehydes formed were separated chromatographically on silica gel using t-butanol - hexane (1:3) as an eluent.

**EXPERIMENTAL**

**Synthesis of oxiranylazines.** A solution of aldehyde (10 mM), trimethylsulfonium chloride (1.35 g, 12 mM), powdered sodium hydroxide (2.0 g, 50 mM) and TEBA (0.05 g) in dry benzene (40 ml) was placed in the glass-stoppered flask and stirred magnetically at room temp. for suitable time (Table 1). The reaction mixture was filtered through Celite and the solvent was evaporated in vacuo. The residue was purified on the column packed with silica gel using chloroform - ethyl acetate (1:1) as an eluent. The crystalline products were recrystallized from hexane. In the case of 2, chromatography was omitted and the crude product was recrystallized from hexane.

2-Oxiranylpyridine and 1-oxiranylisoquinoline were also synthesized in other way. To the vigorously stirred dimethyloxosulfonium methyldide, prepared according to lit. from (CH₃)₂SOCl (1.29 g, 10 mM), the solution of 2-formylpyridine (0.86 g, 8 mM) in dry THF (10 ml) was added dropwise during 15 min. The reaction mixture was diluted with ethyl ether (60 ml) and worked up as described above.

**Synthesis of thiiranylazines.** To a solution of oxiranylazine (5 mM) in ethanol (15 ml), a solution of potassium thiocyanate (0.58 g, 6 mM) in water (5 ml), was added and the reaction mixture was allowed to stand at room temp. for suitable time (Table 2) with occasional stirring. The reaction mixture was diluted with ethyl ether (70 ml) and washed twice with saturated aq. NaCl. A small amount of active carbon was added to the organic layer which was allowed to
stand over anhydrous K₂CO₃. Then solid was filtered off and the solvent was evaporated in vacuo to give crude product which was separated or purified on the column packed with silica gel using chloroform-ethyl acetate (1:1) as an eluent.

Table 1. Oxiranlypyridines, -quinolines and -isoquinolines

<table>
<thead>
<tr>
<th>Compound</th>
<th>Position of substituent</th>
<th>Reaction time, h</th>
<th>Yield %</th>
<th>m.p. °C</th>
<th>(IR CCl₄) a,b</th>
<th>Derivative c</th>
<th>m.p. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>oil</td>
<td>827, 1153, 1240</td>
<td>picr. 110-112</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>3</td>
<td>5</td>
<td>25</td>
<td>oil</td>
<td>820, 1128, 1252</td>
<td>picr. 105-106</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>4</td>
<td>24</td>
<td>15</td>
<td>oil</td>
<td>828, 1150, 1415</td>
<td>picr. 132-134</td>
<td></td>
</tr>
<tr>
<td>2d</td>
<td>2</td>
<td>45 a)</td>
<td>28</td>
<td>oil</td>
<td>860, 1117, 1240</td>
<td>picr. 133</td>
<td></td>
</tr>
<tr>
<td>2e</td>
<td>3</td>
<td>8</td>
<td>38</td>
<td>30-31</td>
<td>850, 1130, 1250</td>
<td>meth. 145</td>
<td></td>
</tr>
<tr>
<td>2f</td>
<td>4</td>
<td>22</td>
<td>57</td>
<td>42</td>
<td>855, 1142, 1238</td>
<td>meth. 119</td>
<td></td>
</tr>
<tr>
<td>2g</td>
<td>5</td>
<td>22</td>
<td>73</td>
<td>25-26</td>
<td>850, 1146, 1235</td>
<td>meth. 126</td>
<td></td>
</tr>
<tr>
<td>2h</td>
<td>6</td>
<td>18</td>
<td>61</td>
<td>16-19</td>
<td>847, 1163, 1250</td>
<td>meth. 138</td>
<td></td>
</tr>
<tr>
<td>2i</td>
<td>7</td>
<td>30</td>
<td>50</td>
<td>25-36</td>
<td>840, 1147, 1249</td>
<td>meth. 136</td>
<td></td>
</tr>
<tr>
<td>2j</td>
<td>8</td>
<td>20</td>
<td>65</td>
<td>59</td>
<td>830, 1170, 1241</td>
<td>picr. 77-78</td>
<td></td>
</tr>
<tr>
<td>2k</td>
<td>1</td>
<td>20</td>
<td>5</td>
<td>36-37</td>
<td>828, 1128, 1240</td>
<td>picr. 126-128</td>
<td></td>
</tr>
<tr>
<td>2l</td>
<td>3</td>
<td>5</td>
<td>33</td>
<td>25</td>
<td>845, 1123, 1240</td>
<td>picr. 128-131</td>
<td></td>
</tr>
</tbody>
</table>

a) Adsorption bands characteristic of the oxirane ring. b) The IR spectra compound 2a-2d were measured in film. c) Picrate - picr., methiodide - meth.

Table 2. Reaction of oxiranlyazines with potassium isothiocyanate

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Reaction time h</th>
<th>Products</th>
<th>Yield %</th>
<th>m.p. °C</th>
<th>Vinylazide</th>
<th>Yield %</th>
<th>m.p. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>95</td>
<td>3a</td>
<td>32</td>
<td>oil a)</td>
<td>4a</td>
<td>0</td>
<td>2g</td>
</tr>
<tr>
<td>2b</td>
<td>20</td>
<td>3b</td>
<td>51</td>
<td>oil a)</td>
<td>4b</td>
<td>0</td>
<td>2h</td>
</tr>
<tr>
<td>2c</td>
<td>46</td>
<td>3c</td>
<td>0 -</td>
<td>oil a)</td>
<td>4c</td>
<td>5</td>
<td>2i</td>
</tr>
<tr>
<td>2d</td>
<td>45</td>
<td>3d</td>
<td>7</td>
<td>oil a)</td>
<td>4d</td>
<td>11</td>
<td>2j</td>
</tr>
<tr>
<td>2e</td>
<td>43</td>
<td>3e</td>
<td>36</td>
<td>72</td>
<td>4e</td>
<td>0</td>
<td>2k</td>
</tr>
<tr>
<td>2f</td>
<td>48</td>
<td>3f</td>
<td>0 -</td>
<td>4f</td>
<td>21</td>
<td>70</td>
<td>3l</td>
</tr>
</tbody>
</table>

a) Easily decomposing at room temp.
Table 3. \( ^1H \) NMR spectra of oxiranylazinines

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>( ^1H ) NMR 100MHz (CCl(_4)), ( \delta(ppm) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>2.99 (1H, dd, J=6 Hz and 2.5 Hz, (-CH_2)-), 3.33 (1H, dd, J=6 Hz and 4 Hz, (-CH_2)-), 4.18 (1H, dd, J=4 Hz and 2.5 Hz, ( \text{H} )), 7.37 (1H, dd, J=8 Hz and 1 Hz, 3-H); 7.42 (1H, dd, J=8 Hz and 1 Hz, 5-H); 7.75 - 7.94 (1H, m, 4-H); 8.70 - 8.76 (1H, m, 6-H).</td>
</tr>
<tr>
<td>2b</td>
<td>2.96 (1H, dd, J=6 Hz and 2.5 Hz, (-CH_2)-), 3.35 (1H, dd, J=6 Hz and 4 Hz, (-CH_2)-), 4.05 (1H, dd, J=4 Hz and 2.5 Hz, ( \text{H} )), 7.44 (1H, dd, J=8 Hz and 4 Hz, 5-H); 7.70 (1H, dd, J=6 Hz and 2 Hz, 4-H); 8.70 - 8.78 (2H, m, 2 and 6-H).</td>
</tr>
<tr>
<td>2c</td>
<td>2.92 (1H, dd, J=6 Hz and 2.5 Hz, (-CH_2)-), 3.36 (1H, dd, J=6 Hz and 4 Hz, (-CH_2)-), 4.00 (1H, dd, J=4 Hz and 2.5 Hz, ( \text{H} )), 7.37 (2H, dd, J=4.5 Hz and 1.5 Hz, 3 and 5-H); 8.74 (2H, dd, J=4.5 Hz and 1.5 Hz, 2 and 6-H).</td>
</tr>
<tr>
<td>2d</td>
<td>3.08 (1H, dd, J=6 Hz and 2.5 Hz, (-CH_2)-), 3.34 (1H, dd, J=6 Hz and 4 Hz, (-CH_2)-), 4.38 (1H, dd, J=4 Hz and 2.5 Hz, ( \text{H} )), 7.52 (1H, d, J=8 Hz, 3-H); 7.62 - 8.00 (3H, m, 5,6 and 7-H); 8.28 (1H, d, J=8 Hz, 4-H); 8.20 - 8.34 (1H, m, 8-H).</td>
</tr>
<tr>
<td>2e</td>
<td>3.03 (1H, dd, J=6 Hz and 2.5 Hz, (-CH_2)-), 3.39 (1H, dd, J=6Hz and 4 Hz, (-CH_2)-), 4.16 (1H, dd, J=4 Hz and 2.5 Hz, ( \text{H} )), 7.55 - 7.98 (3H, m, 5,6 and 7-H); 8.13 (1H, d, J=2 Hz, 4-H); 8.26 -8.36 (1H, m, 8-H); 8.99 (1H, d, J=2 Hz, 2-H).</td>
</tr>
<tr>
<td>2f</td>
<td>2.88 (1H, dd, J=6 Hz and 2.5 Hz, (-CH_2)-), 3.45 (1H, dd, J=6 Hz and 4 Hz, (-CH_2)-), 4.57 (1H, dd, J=4 Hz and 2.5 Hz, ( \text{H} )), 7.48 (1H, d, J=5 Hz, 3-H); 7.62 - 7.98 (2H, m, 6 and 7-H); 8.16 - 8.28 (2H, m, 5 and 8-H); 9.03 (1H, d, J=5 Hz, 2-H).</td>
</tr>
<tr>
<td>2g</td>
<td>2.93 (1H, dd, J=6 Hz and 2.5 Hz, (-CH_2)-), 3.40 (1H, dd, J=6 Hz and 4 Hz, (-CH_2)-), 4.35 (1H, dd, J=4 Hz and 2.5 Hz, ( \text{H} )), 7.56 (1H, dd, J=8 Hz and 4 Hz, 3-H); 7.66 - 7.92 (2H, m, 6 and 7-H); 8.23 (1H, dd, J=8 Hz and 2 Hz, 4-H); 8.60 (1H, dd, J=8 Hz and 2 Hz, 8-H); 9.08 (1H, dd, J=4 Hz and 2 Hz, 2-H).</td>
</tr>
<tr>
<td>2h</td>
<td>2.98 (1H, dd, J=6 Hz and 2.5 Hz, (-CH_2)-), 3.36 (1H, dd, J=6 Hz and 4 Hz, (-CH_2)-), 4.15 (1H, dd, J=4 Hz and 2.5 Hz, ( \text{H} )), 7.54 (1H, dd, J=8 Hz and 4 Hz, 3-H); 7.73 (1H, dd, J=8 Hz and 2 Hz, 7-H); 7.78 (1H, d, J=2 Hz, 5-H); 8.24 (1H, dd, J=8 Hz and 2 Hz, 4-H); 8.28 (1H, d, J=8 Hz, 8-H); 9.05 (1H, dd, J=4 Hz and 2 Hz, 2-H).</td>
</tr>
<tr>
<td>2i</td>
<td>3.01 (1H, dd, J=6 Hz and 2.5 Hz, (-CH_2)-), 3.37 (1H, dd, J=6 Hz and 4 Hz, (-CH_2)-); 4.19 (1H, dd, J=4 Hz and 2.5 Hz, ( \text{H} )), 7.49 (1H, dd, J=8 Hz and 4 Hz, (-CH_2)-); 4.19 (1H, dd, J=4 Hz and 2.5 Hz, ( \text{H} )).</td>
</tr>
</tbody>
</table>
Table 3 (continued)

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>1H NMR 100MHz (CDCl₃), δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2h</td>
<td>2 Hz, J=3-H; 7.53 (1H, d, J=8 Hz, 5-H); 7.99 (1H, d, J=8 Hz, 6-H); 8.18 - 8.30 (2H, m, 4 and 8-H); 9.05 (1H, dd, J=4 Hz and 2 Hz, 2-H).</td>
</tr>
<tr>
<td>2j</td>
<td>2.89 (1H, dd, J=6 Hz and 2.5 Hz, -CH₂-); 3.52 (1H, dd, J=6 Hz and 4 Hz, -CH₂-); 5.22 (1H, dd, J=4 Hz and 2.5 Hz, -C%-), 7.62 (1H, dd, J=8 Hz and 4 Hz, 3-H); 7.70 - 7.96 (3H, m, 5, 6 and 7-H); 8.33 (1H, dd, J=8 Hz and 2 Hz, 4-H); 9.11 (1H, dd, J=4 Hz and 2 Hz, 2-H).</td>
</tr>
<tr>
<td>2k</td>
<td>3.33 (1H, dd, J=6 Hz and 4 Hz, -CH₂-); 3.60 (1H, dd, J=6 Hz and 2.5 Hz, -CH₂-); 4.63 (1H, dd, J=4 Hz and 2.5 Hz, -C%-); 7.68 - 8.04 (4H, m, 4, 5, 6 and 7-H); 8.60 - 8.72 (2H, m, 3 and 8-H).</td>
</tr>
<tr>
<td>2i</td>
<td>3.13 (1H, dd, J=6 Hz and 2 Hz, -CH₂-); 3.37 (1H dd, J=6 Hz and 4 Hz, -CH₂-); 4.30 (1H dd, J=4 Hz and 2 Hz, -C%-); 7.70 - 8.20 (5H, m, 4, 5, 6, 7 and 8-H); 9.36 (1H, a, 1-H).</td>
</tr>
</tbody>
</table>

Table 4. ¹H NMR spectra of thiopyrinalazine and vinylquinolines

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>¹H NMR 100MHz (CDCl₃), δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jₙ</td>
<td>3.04 (1H, dd, J=6.5 Hz and 1 Hz, -CH₂-); 3.19 (1H, dd, J=5.5 Hz and 1 Hz, -CH₂-); 4.19 (1H, dd, J=6.5 Hz and 5.5 Hz, -C%-); 7.26 - 7.52 (2H, m, 3-H and 5-H); 7.70 - 7.90 (1H, m, 4-H); 8.64 - 8.74 (1H, m, 6-H).</td>
</tr>
<tr>
<td>Dₙ</td>
<td>2.95 (1H, dd, J=6 Hz and 1.5 Hz, -CH₂-); 3.24 (1H, dd, J=6 Hz and 1.5 Hz, -CH₂-); 4.20 (1H, t, J=6 Hz, -CH₂-); 7.56 (1H, dd, J=8 Hz and 4.5 Hz, 5-H); 7.94 (1H dt, J=8 Hz and 2 Hz, 4-H); 8.82 (1H, dd, J=4.5 Hz and 2 Hz 6-H); 8.92 (1H, d, J=2 Hz, 2-H).</td>
</tr>
<tr>
<td>Dₙ</td>
<td>3.12 - 3.30 (2H, m, -CH₂-); 4.42 (1H, t, J=6 Hz, -CH₂-); 7.45 (1H, d, J=8 Hz, 3-H); 7.66 - 7.99 (3H, m, 5, 6 and 7-H); 8.23 (1H, d, J=8 Hz, 4-H); 8.16 - 8.32 (1H, m, 8-H).</td>
</tr>
</tbody>
</table>
| Jₙ        | 2.90 (1H, dd, J=6 Hz and 1.5 Hz, -CH₂-); 3.10 (1H, dd, J=6 Hz and 1.5 Hz, -CH₂-); 4.16 (1H, t, J=6 Hz, -C%-); 7.60 - 7.93 (3H, m, 5, 6 and 7-H); 8.07 (1H, d, J=2 Hz, 4-H); 8.13 - 8.33 (1H, m, 8-H); 8.94 (1H, d, J=2 Hz, 2-H); 3.12 (1H, dd, J=6 Hz and 1.5 Hz, -CH₂-); 3.34 (1H, dd, J=6 Hz and 1.5 Hz, -CH₂-); 4.76 (1H, t, J=6 Hz, -CH₂-); 7.76 - 8.06 (3H, m, 3, 6 and 7-H); 8.34 - 8.45 (1H, m, 4-H); 8.94 - 9.06 (1H, m, 8-H); 9.26 - 9.34 (1H, m, 2-H); 3.02 (1H, dd, J=6 Hz and 1.5 Hz, -CH₂-); 3.24 (1H, dd, J=6 Hz and 1.5 Hz, -CH₂-); 4.33 (1H, t, J=6 Hz, -CH₂-); 7.59 (1H, dd, J=8 Hz and 4 Hz, 3-H); 7.80 (1H, dd, J=9 Hz and 2 Hz, 7-H); 8.02 (1H, d, J=2 Hz, 5-H); 8.28 - 8.40
Table 4 (continued)

| 2h | (2H, m, 4 and 8-H); 9.17 (1H, dd, J=4 Hz and 2 Hz, 2-H). 2.95 (1H, dd, J=6 Hz and 1.5 Hz, -CH$_2$-); 3.16 (1H, dd, J=6 Hz and 1.5 Hz, -CH$_2$-); 4.28 (1H, t, J=6 Hz, 3); 7.44 - 7.62 (2H, m, 3 and 5-H); 7.88 (1H, d, J=8 Hz, 6-H); 8.18 - 8.34 (2H, m, 4 and 8-H); 9.04 - 9.12 (1H, m, 2-H). 2.80 (1H, dd, J=6 Hz and 1.5 Hz, -CH$_2$-); 3.13 (1H, dd, J=6 Hz and 1.5 Hz, -CH$_2$-); 5.45 (1H, t, J=6 Hz, S); 7.68 (1H, dd, J=8 Hz and 4 Hz, 3-H); 7.68 - 7.90 (3H, m, 5, 6 and 7-H); 8.27 (1H, dd, J=8 Hz and 2 Hz, 4-H); 9.11 (1H, dd, J=4 Hz and 2 Hz, 2-H). 3.09 (1H, d, J=6.5 Hz, -CH$_2$-); 4.01 (1H, d, J=5.5 Hz, -CH$_2$-); 4.76 (1H, dd, J=6 Hz and 5.5 Hz, S). |
| 3j | 7.70 - 8.10 (4H, m, 4, 5, 6 and 7-H); 8.57 - 8.72 (2H, m, 3 and 8-H). 3.09 (1H, d, J=6.5 Hz, -CH$_2$-); 3.40 (1H, d, J=5.5 Hz, -CH$_2$-); 4.34 (1H, dd, J=6 Hz and 5.5 Hz, S); 7.71 - 8.20 (5H, m, 4, 5, 6, 7 and 8-H); 9.35 (1H, s, 1-H). |
| 3k | 5.80 (1H, dd, J=12 Hz and 2 Hz, =CH$_2$); 6.47 (1H, dd, J=18 Hz and 2 Hz, =CH$_2$); 7.20 (1H, dd, J=18 Hz and 12 Hz, =CH$_2$); 7.60 - 7.96 (4H, m, 3, 5, 6 and 7-H); 8.19 (1H, d, J=8 Hz, 4-H); 8.14 - 8.34 (1H, m, 8-H). |
| 3l | 5.86 (1H, dd, J=11 Hz and 2 Hz, =CH$_2$); 6.14 (1H, dd, J=18 Hz and 2 Hz, =CH$_2$); 7.45 - 8.00 (4H, m, =CH$_2$, 3, 6 and 7-H); 8.22 - 8.42 (2H, m, 5 and 8-H); 9.06 (1H, d, J=5 Hz, 2-H). |

REFERENCES AND NOTES


8. 2- and 4-vinylpyridine were synthesized by E. Sh. Kagan and B.I. Ardashev, Khim.Geterotsikl.Sed., 1967, 701, but no $^1$H NMR data were reported.


11. All new compounds gave satisfactory microanalyses for C, H, N and S (thiiranes) within 0.3%.

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