of methyl \( N \)-aryldithiocarbamates (1) under reduced pressure to afford the corresponding aryl isothiocyanates in up to 84% yield\(^1\). One of the better methods for the preparation of aryl isothiocyanates is the decomposition of ethoxycarbonyl \( N \)-aryldithiocarbamates\(^2\) but the starting materials are unstable and are usually prepared \textit{in situ} from the ammonium dithiocarbamate (or amine hydrochloride + carbon disulfide + sodium hydroxide) and ethyl carbonochloridate\(^3\).

In connection with our investigations on the synthesis of substituted thiazoles, we have found that the base-catalyzed decomposition of methyl \( N \)-aryldithiocarbamates 1 gives the aryl isothiocyanates 2 in good yields under relatively mild conditions and in a simple operation.

\[
\text{R-NH-C-S-CH}_3 \xrightarrow{\text{NaOH/toluene}} \text{R-N=C=S} + \text{H}_2\text{C-SH}
\]

Thus, a toluene solution of the dithiocarbamate 1 is treated with solid sodium hydroxide and the mixture is heated under reflux for 1-2 h to give the isothiocyanates 2 after a simple work-up. The products 2 are usually sufficiently pure for further reactions and can be obtained in analytical purity by short-path distillation under reduced pressure or by recrystallization from hexane (Table).

Melting points were measured using a Thomas Hoover melting point apparatus. \(^1\)H-N.M.R. spectra were recorded on a Varian FT-80A spectrometer, and I.R. spectra with a Perkin-Elmer 283 instrument. The methyl \( N \)-aryldithiocarbamates 1 were prepared according to Ref.\(^6\) and are stable, crystalline solids.

2-Methylphenyl Isothiocyanate (2b); Typical Procedure:
To a solution of methyl \( N \)-(2-methylphenyl)-dithiocarbamate (1b; 9.85 g, 50 mmol) in toluene (30 ml) is added solid, finely divided sodium hydroxide (80 mg, 2 mmol). The mixture is slowly heated to reflux with vigorous stirring under a gentle stream of dry nitrogen to remove methanol (3). After 2 h, the mixture is cooled to room temperature and washed with water (3 x 10 ml). The organic solvent is evaporated under reduced pressure and the residue distilled in vacuo to give the product as a light colored oil; yield: 7.01 g (94%); b.p. 92-95 °C/3.0 torr; homogeneous by thin layer chromatography on silica gel, solvent: hexane/ether (1:1).

A Facile, Modified Synthesis of Aryl Isothiocyanates from Methyl \( N \)-Aryldithiocarbamates

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Numerous methods for the synthesis of isothiocyanates have been reported\(^1\). One of these methods involves the pyrolysis

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Table. Aryl Isothiocyanates 2 prepared

<table>
<thead>
<tr>
<th>Product No.</th>
<th>R</th>
<th>Reaction time</th>
<th>Yield [%]</th>
<th>m.p. [°C] or b.p. [°C]/torr</th>
<th>l.R. (AgBr)</th>
<th>(\nu_{\text{C-S}}) [cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td></td>
<td>1.5 h</td>
<td>93</td>
<td>65-67°/3.5</td>
<td>105-108°/14°</td>
<td>2085</td>
</tr>
<tr>
<td>2b</td>
<td></td>
<td>2 h</td>
<td>94</td>
<td>92-95°/3.0</td>
<td>126-129°/12°</td>
<td>2085</td>
</tr>
<tr>
<td>2c</td>
<td>H(_2)C</td>
<td>2 h</td>
<td>90</td>
<td>110-113°/5.0</td>
<td>129-132°/12°</td>
<td>2080</td>
</tr>
<tr>
<td>2d</td>
<td>H(_2)C</td>
<td>1.5 h</td>
<td>90</td>
<td>90-92°/4.0</td>
<td>130-133°/25°</td>
<td>2095</td>
</tr>
<tr>
<td>2e</td>
<td>Cl</td>
<td>1 h</td>
<td>91</td>
<td>45-46°</td>
<td>46.5-46°</td>
<td>2070</td>
</tr>
<tr>
<td>2f</td>
<td>H(_2)CO</td>
<td>1.5 h</td>
<td>93</td>
<td>126-129°/3.0</td>
<td>156-158°/24°</td>
<td>2095</td>
</tr>
<tr>
<td>2g</td>
<td>Cl</td>
<td>2 h</td>
<td>92</td>
<td>115-118°/4.7</td>
<td>--</td>
<td>2080</td>
</tr>
<tr>
<td>2h</td>
<td>C(_2)H(_5)</td>
<td>1.5 h</td>
<td>96</td>
<td>109-112°/4.7</td>
<td>--</td>
<td>2095</td>
</tr>
<tr>
<td>2i</td>
<td></td>
<td>1.5 h</td>
<td>90</td>
<td>54-55°</td>
<td>58-59°</td>
<td>2080</td>
</tr>
</tbody>
</table>

a Yield of pure isolated product, homogeneous by thin layer chromatography (silica gel).

b Not corrected.

c C\(_{18}\)H\(_{18}\)C\(_8\)N\(_3\)S\(_4\) calc. C 52.37 H 3.29 N 7.63 S 17.45 (183.7) found 52.40 3.31 7.15 17.40

d C\(_{12}\)H\(_{16}\)N\(_3\)S\(_4\) calc. C 69.07 H 6.85 N 7.32 S 16.76 (191.3) found 69.47 6.59 7.25 16.50

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5 Ref. 1, p. 870.