

## Preparation of $\beta$ -Alkylimino-dithiocarboxylic Acids

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The title compounds were prepared by the reaction of carbon disulphide with the product obtained by refluxing a mixture of a ketone and a primary amine with potassium fluoride. Ketones in which  $\alpha$ -position is sterically hindered were reluctant to undergo this reaction.

SYNTHESES of  $\beta$ -alkylimino-dithiocarboxylic acids and related compounds have been reported previously.<sup>1,2</sup> The procedure involved treatment of *N*-alkylimino-compounds, prepared from *gem*-dithiols, with carbon disulphide. We have reported that 2-iminocyclopentanedithiocarboxylic acid can be prepared easily from cyclopentanone and carbon disulphide in the presence of ammonia.<sup>3</sup> Recently this reaction has been

carried out with methylamine in place of ammonia.<sup>4</sup> This extension, however, was limited to methylamine; other 2-alkyliminocyclopentanedithiocarboxylic acids were prepared from the imino-acid by an amine exchange reaction. This method thus requires the isolated imino-dithiocarboxylic acids as starting materials, and only a few examples of these are now known.<sup>3,5,6</sup>

<sup>1</sup> R. Mayer and J. Jentsch, *J. prakt. Chem.*, 1964, **23**, 83.

<sup>2</sup> R. Gompper, B. Wetzler, and W. Elser, *Tetrahedron Letters*, 1968, 5519.

<sup>3</sup> T. Takeshima, M. Yokoyama, T. Imamoto, M. Akano, and H. Asaba, *J. Org. Chem.*, 1969, **34**, 730.

<sup>4</sup> B. Bordás, P. Sohár, G. Matolcsy, and P. Berencsi, *J. Org. Chem.*, 1972, **37**, 1727.

<sup>5</sup> G. Matolcsy, P. Sohár, and B. Bordás, *Chem. Ber.*, 1971, **104**, 1155.

<sup>6</sup> T. Takeshima, T. Miyauchi, N. Fukada, S. Koshizawa, and M. Muraoka, *J.C.S. Perkin I*, 1973, 1009.

2-Alkyliminocyclopentanedithiocarboxylic acids <sup>a</sup> and 2,4-dinitrophenyl esters of (2a) and (4a)—(11a)

| Compound          | Yield (%) | M.p. (°C)  | $\lambda_{\max.}/\text{nm}$<br>(log $\epsilon$ ) <sup>b</sup> | Formula  | Found (%) |      |      |       | Calc. (%) |      |      |      |
|-------------------|-----------|--|---|--|-----------|------|------|-------|-----------|------|------|------|
|                   |           |  |   |  | C         | H    | N    | S     | C         | H    | N    | S    |
| (1a)              | 29        | 101—102  | 303 (3.91)  | C <sub>10</sub> H <sub>17</sub> NS <sub>2</sub>                              | 56.2      | 8.0  | 6.45 | 29.8  | 55.8      | 8.0  | 6.5  | 29.7 |
| (2a)              | 16        | 49—50  | 396 (4.32)  | C <sub>12</sub> H <sub>21</sub> NS <sub>2</sub>                              | 59.5      | 8.4  | 5.8  | 26.3  | 59.2      | 8.7  | 5.8  | 26.3 |
| (3a)              | 61        | 101—103  | 303 (3.87)  | C <sub>12</sub> H <sub>19</sub> NS <sub>2</sub>                              | 59.8      | 7.6  | 5.8  | 26.5  | 59.7      | 7.9  | 5.8  | 26.5 |
| (4a) <sup>c</sup> | 31        | 78—79  | 303 (3.95)  | C <sub>13</sub> H <sub>21</sub> NS <sub>2</sub>                              | 61.3      | 8.2  | 5.65 | 25.0  | 61.15     | 8.3  | 5.5  | 25.1 |
| (5a)              | 45        | (decomp.)  | 398 (4.44)  |  |           |      |      |       |           |      |      |      |
| (2b)              |           | 113—114  | 392 (4.40)  | C <sub>18</sub> H <sub>23</sub> N <sub>3</sub> O <sub>4</sub> S <sub>2</sub> | 53.15     | 5.6  | 10.3 | 15.45 | 52.8      | 5.7  | 10.3 | 15.6 |
| (4b)              |           | 146—147 <sup>d</sup>                               | 424sh (3.87)  |  |           |      |      |       |           |      |      |      |
| (5b)              |           | (Me <sub>2</sub> N·CHO—MeOH—H <sub>2</sub> O)      | 393 (4.33)  | C <sub>17</sub> H <sub>21</sub> N <sub>3</sub> O <sub>4</sub> S <sub>2</sub> | 51.9      | 5.35 | 10.4 | 16.5  | 51.6      | 5.35 | 10.6 | 16.2 |
| (6b)              |           | 145—146 <sup>e</sup>                               | 409sh (4.23)  |  |           |      |      |       |           |      |      |      |
| (7b)              |           | (Me <sub>2</sub> N·CHO—MeOH—H <sub>2</sub> O)      | 392 (4.30)  | C <sub>19</sub> H <sub>23</sub> N <sub>3</sub> O <sub>4</sub> S <sub>2</sub> | 54.3      | 5.5  | 9.8  | 15.3  | 54.1      | 5.5  | 10.0 | 15.2 |
| (8b)              |           | 138—139  | 412sh (4.23)  |  |           |      |      |       |           |      |      |      |
| (9b)              |           | (Me <sub>2</sub> N·CHO—H <sub>2</sub> O)           | 378 (4.25)  | C <sub>17</sub> H <sub>21</sub> N <sub>3</sub> O <sub>4</sub> S <sub>2</sub> | 51.8      | 5.35 | 10.4 | 16.4  | 51.6      | 5.35 | 10.6 | 16.2 |
| (10b)             |           | 111—112  | 414sh (4.09)  |  |           |      |      |       |           |      |      |      |
| (11b)             |           | (Me <sub>2</sub> N·CHO—MeOH)                       | 378 (4.22)  | C <sub>19</sub> H <sub>23</sub> N <sub>3</sub> O <sub>4</sub> S <sub>2</sub> | 54.05     | 5.95 | 9.8  | 15.4  | 53.9      | 5.95 | 9.9  | 15.1 |
| (1a)              |           | 146—147  | 414sh (4.07)  |  |           |      |      |       |           |      |      |      |
| (2a)              |           | (EtOH) (decomp.)                                   | 416sh (4.13)  |  |           |      |      |       |           |      |      |      |
| (3a)              |           | 125—126  | 378 (4.22)  | C <sub>20</sub> H <sub>27</sub> N <sub>3</sub> O <sub>4</sub> S <sub>2</sub> | 54.9      | 6.2  | 9.4  | 14.7  | 54.9      | 6.2  | 9.6  | 14.7 |
| (4a)              |           | (Me <sub>2</sub> N·CHO—MeOH)                       | 417sh (4.07)  |  |           |      |      |       |           |      |      |      |
| (5a)              |           | 143—144  | 378 (4.25)  | C <sub>20</sub> H <sub>25</sub> N <sub>3</sub> O <sub>4</sub> S <sub>2</sub> | 55.2      | 5.8  | 9.4  | 14.9  | 55.15     | 5.8  | 9.65 | 14.7 |
| (6a)              |           | (Me <sub>2</sub> N·CHO—H <sub>2</sub> O) (decomp.) | 414sh (4.10)  |  |           |      |      |       |           |      |      |      |
| (7a)              |           | 148—149 <sup>f</sup>                               | 393 (4.30)  | C <sub>19</sub> H <sub>24</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub> | 52.4      | 5.6  | 12.7 | 14.7  | 52.3      | 5.5  | 12.8 | 14.7 |
| (8a)              |           | (Me <sub>2</sub> N·CHO—EtOH)                       | 409sh (4.23)  |  |           |      |      |       |           |      |      |      |

<sup>a</sup> Compounds (1a)—(3a) and (5a) absorbed at  $\nu_{\max.}$  2445—2470 (SH) and 1595—1610  $\text{cm}^{-1}$  (C=N). Yields of compounds (2b)—(11b) were almost theoretical. <sup>b</sup> In EtOH. <sup>c</sup> Compound (4a) was of low m.p. and tended to form an oil; it was therefore characterised as the 2,4-dinitrophenyl ester (4b). <sup>d</sup> Rapid heating, *ca.* 156°. <sup>e</sup> Rapid heating, *ca.* 159°. <sup>f</sup> Rapid heating, *ca.* 160°.

We now report a simple and general method of preparing  $\beta$ -alkylimino-dithiocarboxylic acids, involving addition of carbon disulphide to the product obtained by

refluxing a mixture of carbonyl compound and primary amine with anhydrous potassium fluoride. The addition of the latter had a marked effect in assisting the dehydration. Three procedural variations were employed (methods A—C in the Experimental section).

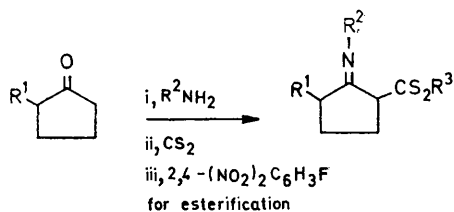
Cyclopentanone, 2-methylcyclopentanone, cyclohexanone, 3-methylcyclohexanone, and *N*-methyl-4-piperidone afforded the imino-acids (1a)—(11a). Of these, compounds (6a)—(10a), which were unstable, were converted into the 2,4-dinitrophenyl esters (6b)—(10b). Some of the other imino-acids were also converted into the esters. The results are summarised in the Table.

Ketones in which  $\alpha$ -position is sterically hindered were reluctant to undergo the reaction. This may be due to difficulty in the formation of the ketimine, or to hindrance to the attack of carbon disulphide on the ketimine. Thus, the desired products could not be isolated from the reactions of diethyl ketone, isopropyl methyl ketone, and 2-methylcyclohexanone. Ethyl methyl ketone, which affords the corresponding thiazine in the reaction with carbon disulphide in the presence of ammonia,<sup>7</sup> seemed to react sluggishly in the present case. On the other hand, 3-methylcyclohexanone, which fails to react with carbon disulphide in the presence of ammonia,<sup>8</sup> gave the expected product in the present reaction.

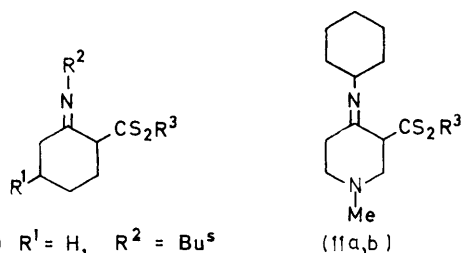
All the imino-acids reported here were exceedingly sensitive to Ni<sup>II</sup> ion, giving a pink-red precipitate.

<sup>7</sup> T. Takeshima, T. Imamoto, M. Yokoyama, K. Yamamoto, and M. Akano, *J. Org. Chem.*, 1968, **33**, 2877.

<sup>8</sup> T. Takeshima, T. Hayashi, M. Muraoka, and T. Matsuoka, *J. Org. Chem.*, 1967, **32**, 980.



- (1a) R<sup>1</sup> = H, R<sup>2</sup> = Bu<sup>s</sup>  
 (2a,b) R<sup>1</sup> = H, R<sup>2</sup> = *n*-C<sub>6</sub>H<sub>13</sub>  
 (3a) R<sup>1</sup> = H, R<sup>2</sup> = *cyclo*-C<sub>6</sub>H<sub>11</sub>  
 (4a,b) R<sup>1</sup> = Me, R<sup>2</sup> = Bu<sup>s</sup>  
 (5a,b) R<sup>1</sup> = Me, R<sup>2</sup> = *cyclo*-C<sub>6</sub>H<sub>11</sub>



a; R<sup>3</sup> = H b; R<sup>3</sup> = 2,4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>

## EXPERIMENTAL

All the  $\beta$ -alkylimino-dithiocarboxylic acids (1a)—(11a) could be prepared by method A, B, or C. Especially pure products were obtained by method B. These imino-acids were sensitive to oxidation; recrystallisation was therefore conducted in the cold.

*$\beta$ -Alkylimino-dithiocarboxylic Acids.—Method A.* A mixture of ketone (0.06 mol) and alkylamine (0.06 mol) was refluxed with anhydrous potassium fluoride (0.06 mol) for 2–5 h. The potassium fluoride was then filtered off and carbon disulphide (0.12 mol) was gradually added to the filtrate, below 0°, with stirring. The yellow precipitate was collected, washed with ether, dried, and recrystallised (see Table).

*$\beta$ -Alkyliminocyclohexanedithiocarboxylic acids (6a)—(10a) and 4-cyclohexylimino-*N*-methylpiperidine-3-dithiocarboxylic acid (11a)* were obtained in yields of *ca.* 40–60%.

*Method B.* The pure ketimine was isolated after the refluxing stage by fractionation under reduced pressure. It was then diluted with an inert solvent such as ether, and treated as in A.

*Method C.* Unchanged amine was removed after the refluxing stage by distillation under reduced pressure. The residue was then treated as in A.

*2,4-Dinitrophenyl  $\beta$ -Alkylimino-dithiocarboxylates.*—To a solution of  $\beta$ -alkylimino-dithiocarboxylic acid (0.02 mol) in ether (200–300 ml) was added triethylamine (0.03 mol), followed by 2,4-dinitrofluorobenzene (0.03 mol), below 0°. The mixture was kept for 1–2 h in an ice-bath. The orange solid product was collected, washed with methanol, dried (yield 75–95%), and recrystallised (see Table).

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