

## Synthesis and Isomerization Studies of 2-Alkenylthiopyrimidines and 2-Alkynylthiopyrimidines and Their S-Oxides

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Selective oxidations for the preparation of either sulfoxides or sulfones of 2-allyl, 2-propadienyl- and 2-propargylthio-5-chloropyrimidines are described. The 2-propargylsulfone as well as its sulfide is easily isomerized to the isomeric allenes. The unsaturated sulfides are conveniently prepared in a condensation reaction between 1,3-bis-*N,N*-dimethylamino-2-chlorotrimethinium perchlorate and the respective isothioureas.

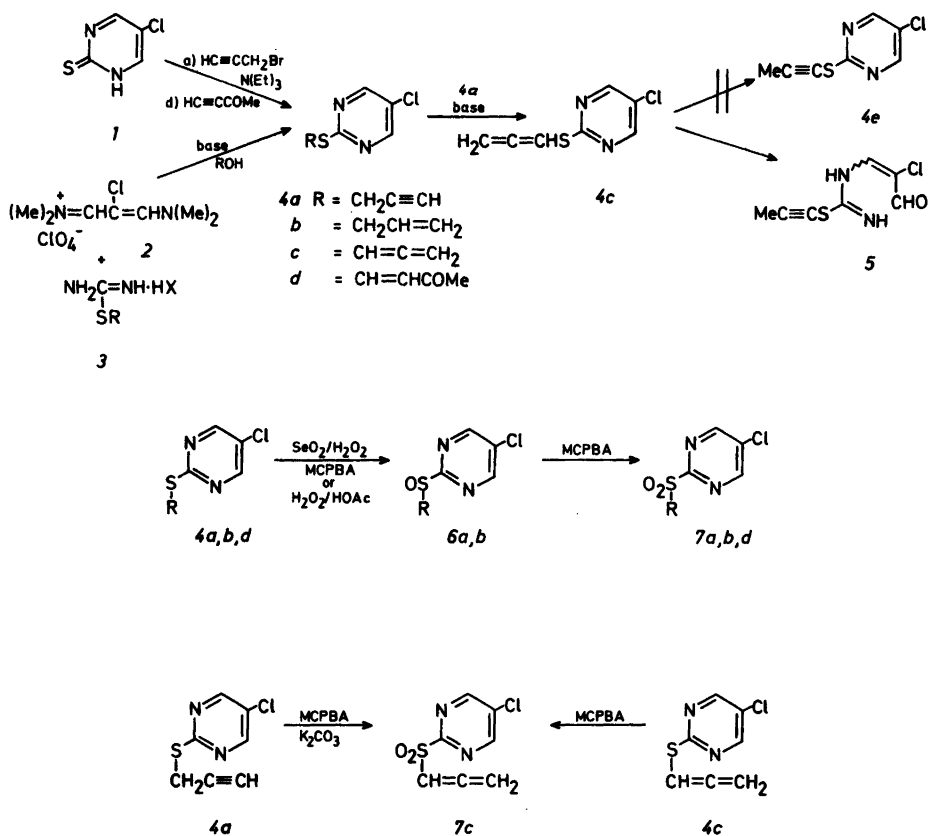
Recently we reported syntheses and properties of some  $\alpha$ -haloalkyl pyrimidine sulfides and their oxides.<sup>1</sup> Herein we describe studies of propargyl and alkenyl 2-pyrimidine sulfides and of their reactivity towards oxidizing agents.

2-Alkylthiopyrimidines can be prepared by *S*-alkylation of 2-mercaptopyrimidines,<sup>2a</sup> by the reaction of alkylmercaptide salts with pyrimidines containing mobile 2-substituents,<sup>2b</sup> or by the condensation of a three-carbon unit with *S*-alkylisothioureas.<sup>2c</sup> Thus, 2-propargylthiopyrimidine **4a** is formed in good yield from the 2-mercaptopyrimidine **1** and propargyl bromide under basic conditions. The *S*-vinyl derivative **4d** was prepared in a Michael reaction between **1** and the activated triple bond in ethynyl methyl ketone, this reaction being analogous to those we have reported for pyridine-2-thiones and activated acetylenic compounds.<sup>3</sup> Compound **4d** was obtained as a 1:1 stereoisomer mixture.

Since the route to the mercaptide starting material **1** is relatively lengthy,<sup>4</sup> condensation reactions between isothioureas and the trimethinium salt **2** have been explored as an alternative route to the preparation of **4**. The propargyl isothioureas **3a** can be prepared by alkylation of thiourea with propargyl bromide in ethanol.<sup>5</sup> We find, however,

that if the reaction at 80°C is left for more than 5–10 min increasing amounts of the isomeric propadienylisothioureas **3c** are formed. In 1,2-dimethoxyethane solution, however, no isomerization was observed when the reaction mixture was kept at 50°C for 24 h, the yield being in excess of 90%.

The trimethinium salt **2** is equivalent to 2-chloromalondialdehyde. It is readily available and is an excellent reactant in the formation of 5-chloropyrimidines by condensation reactions.<sup>6,7</sup> Thus both the propargyl- and the allyl-isothioureas **3** underwent condensation with the trimethinium salt **2** under basic conditions to form **4**. Heating is to be avoided in the case of the propargylisothioureas, because of its ready isomerization with formation of the 2-propadienylthiopyrimidine **4c**. Only the latter isomer together with decomposition products was formed in the presence of excess base. The ready base-catalyzed isomerization of propargyl sulfides has been rationalized by good stabilization of the intermediate carbanion by the ability of sulfur to expand its outer electron shell from eight to ten electrons.<sup>8</sup> The deprotonation rate is much higher for propargyl than for propadienyl thioethers,<sup>9</sup> and hence it should be possible to obtain relatively pure propadienylthioethers. This proved to be the case for the propadienyl thioether **4c** which was readily prepared on treatment of the propargyl thioether **4a** with 0.1 equivalent of *tert*-butoxide in *tert*-butanol. The crude product of the isomer **4c** also contained some ring-opened substance formulated as the isomer **5** (NMR; 15%). With potassium *tert*-butoxide added to ethanol, however, there was no detectable isomerization of **4a** to **4c** after the solution had been kept at 60°C for 2 days. This is notable since phenyl propargyl sulfide is rapidly isomerized (30 min.; 89%) under



milder conditions.<sup>10</sup> This difference, perhaps in the opposite direction of what was to be expected on electronic grounds, may be rationalized by involving the lone pair of electrons on the nitrogen atoms; charge repulsion by the electrons will reduce the rate of proton abstraction by the approaching base. Support for this view can be found in the arguments used to explain that nucleophilic substitution in the pyrimidine 2-position is slower than in the 4-position.<sup>11,12</sup>

In no case did the isomerization reaction proceed to the 1-propynyl sulfide 4e in contrast to phenyl propargyl sulfide which is readily isomerized to phenyl 1-propynyl sulfide.<sup>10</sup>

Acetylenic sulfoxides and sulfones can be prepared by oxidation of the corresponding sulfides.<sup>13,14</sup> In the case of 4a formation of its sulfoxide 6a was very slow when using sodium metaperiodate in methanol; selective oxidation with *m*-chloroperbenzoic acid (MCPBA) was difficult to achieve. The cleanest oxidation was observed by the use of

selenium dioxide in hydrogen peroxide when the sulfoxide 6a was isolated in satisfactory yield (63 %).

In the oxidation of the propargyl sulfide 4a to sulfone using MCPBA, either the propargyl sulfone 7a or the propadienyl sulfone 7c could be isolated depending on the isolation procedure; neutralization of the reaction mixture with 1 M sodium bicarbonate gave the propargyl sulfone 7a whereas treatment with saturated potassium carbonate solution gave the propadienyl sulfone 7c, and with 1 M sodium carbonate solution a mixture of the isomers was obtained. Very ready base-catalyzed isomerization is also what has been reported for aryl propargyl sulfones,<sup>13</sup> and it has been shown that aryl propadienyl sulfones are thermodynamically more stable than their acetylenic isomers.<sup>15</sup> The propadienyl sulfone 7c can also be prepared by direct oxidation of the allene 4c using MCPBA.

Selective sulfoxide formation from the allyl sulfide 4b was readily achieved using hydrogen peroxide in acetic acid as reported for simple allyl phenyl

sulfides.<sup>16</sup> For the selective oxidation to the sulfone 7b, MCPBA rather than hydrogen peroxide in acetic acid<sup>17</sup> was the preferred reagent.

The *S*-vinyl derivative 4d can also be selectively *S*-oxidized. Thus its 1:1 stereoisomer mixture with MCPBA was converted to the sulfone 7d and the (*Z*)- and (*E*)-isomers were separated by preparative TLC.

## EXPERIMENTAL

**2-Propargylthiouronium bromide 3a.** A mixture of propargylbromide (1.19 g, 10 mmol) and thiourea (0.76 g, 10 mmol) in dimethoxyethane (20 ml) was heated at 50 °C for 15 h. The solvent was distilled off and the residue washed with ether. The product was recrystallized from acetone-pentane; yield 1.85 g (95%), m.p. 124 °C.<sup>10</sup>

**5-Chloro-2-propargylthiopyrimidine 4a.** *Method A.* Potassium *tert*-butoxide (4.48 g, 40 mmol) in abs. ethanol (40 ml) was added dropwise over 10 min. to a mixture of 2-propargylthiouronium bromide (3.92 g, 20 mmol) and 1,3-bis-*N,N*-dimethylamino-2-chlorotrimethinium perchlorate<sup>18</sup> (5.33 g, 20 mmol) in abs. ethanol (80 ml). The mixture was stirred for 48 h at room temperature before the solvent was distilled off. The residue was washed with water, extracted into chloroform, dried (MgSO<sub>4</sub>) and evaporated. The product was recrystallized from methanol-water; yield 2.44 g (66%), m.p. 66 °C. Anal. C<sub>7</sub>H<sub>5</sub>ClN<sub>2</sub>S: C, H. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.16 (HC, t, *J* 2 Hz), 3.88 (≡CCH<sub>2</sub>, d, *J* 2 Hz), 8.50 (H-4, H-6). IR (KBr): 3300 (≡CH), 1550 cm<sup>-1</sup> (pyrimidine). MS[70 eV, *m/z* (% rel. int.)]: 186/184 (33/100, M), 150(33), 114(28), 71(30), 39(56).

*Method B.* A mixture of 5-chloropyrimidine-2-thione (0.73 g, 5 mmol) and triethylamine (0.70 ml, 5 mmol) was stirred together in dichloromethane (40 ml) for 5 min before propargyl bromide (0.71 g, 6 mmol) was added. The mixture was stirred at room temperature for 1 h and subsequently the solvent was evaporated. The residue was triturated with water (20 ml), and the solid recrystallized from methanol; yield: 0.80 g (87%).

**2-Allylthio-5-chloropyrimidine 4b.** 1,3-Bis-*N,N*-dimethylamino-2-chlorotrimethinium perchlorate<sup>18</sup> (8.0 g, 31 mmol) and 2-allylthiouronium bromide<sup>19</sup> (6.90 g, 35 mmol) were dissolved in methanol (80 ml) and methanolic 1.67 M sodium methoxide (35 mmol) was added. The mixture was stirred at room temperature for 30 min before additional sodium methoxide solution (19 ml; 31 mmol) was added. The mixture was then heated under reflux for 2.5 h, the solvent distilled off, water (100 ml) added to the residue, the mixture extracted with chloroform,

the dried (MgSO<sub>4</sub>) chloroform solution evaporated, and the residue distilled; yield 5.0 g (86%), b.p. 62–64 °C/0.1 mmHg. Anal. C<sub>7</sub>H<sub>7</sub>ClN<sub>2</sub>S: C, H. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.76 (CH<sub>2</sub>-S), 5.0–6.4 (vinyl), 8.40 (H-4, H-6). IR (film): 1560 and 1530 cm<sup>-1</sup> (pyrimidine). MS[70 eV, *m/z* (% rel. int.)]: 188/186 (9/25, M) 173(38), 171(100), 155(16), 153(46), 118(22), 114(21).

**5-Chloro-2-propadienylthiopyrimidine 4c.** Potassium *tert*-butoxide (44 mg, 0.4 mmol) was added to a solution of 5-chloro-2-propargylthiopyrimidine (0.74 g, 4 mmol) in *tert*-butanol. The mixture was stirred at room temperature for 90 min before water (100 ml) was added and the solution was extracted with chloroform. The dried (MgSO<sub>4</sub>) chloroform solution was evaporated and the crude product purified on a silica gel column (chloroform-light petroleum; 1:1); yield 0.40 g (54%), m.p. 32–34 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.00 (H<sub>2</sub>C=, *J* 6 Hz), 6.45 (=CH-S, *J* 6 Hz), 8.36 (H-4, H-6). IR (KBr): 1940 (allene), 1550 and 1520 cm<sup>-1</sup> (pyrimidine). MS[70 eV, *m/z* (% rel. int.)]: 154 (10, M), 149(1), 114(2), 71(4), 70(2), 43(15). The product was chromatographically homogeneous and was directly oxidized to the corresponding sulfone because it appeared to decompose (colouration) on storage.

**5-Chloro-2-(3-oxobuten-1-yl)thiopyrimidine 4d.** 3-Butyn-2-one<sup>20</sup> (0.34 g, 5 mmol) in chloroform (25 ml) was added dropwise over 10 min at room temperature to a stirred suspension of 5-chloropyrimidine-2-thione (0.66 g, 4.5 mmol) in chloroform (25 ml). The mixture was stirred for an additional 10 min before the solvent was evaporated. The residue was crystallized from methanol; yield 0.70 g (72%), m.p. 89 °C. Anal. C<sub>8</sub>H<sub>7</sub>ClN<sub>2</sub>OS: C, H. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.20 (Me-(*Z*)), 2.23 (Me-(*E*)), 6.52 (H<sub>α</sub>, d, *J* 18 Hz (*E*)), 6.58 (H<sub>α</sub>, d, *J* = 10 Hz (*Z*)), 8.43 (H<sub>β</sub>, d, *J* 10 Hz) (*Z*)), 8.57 (H<sub>β</sub>, d, *J* 18 Hz (*E*)), 8.62 (H-4, H-6); (*E*)/(*Z*)=1:1. IR (KBr): 1660 cm<sup>-1</sup> (CO). MS[70 eV, *m/z* (% rel. int.)]: 216/214 (2/6, M), 199(4), 173(37), 171(100).

**1-(2-Chloro-3-oxo-1-propenyl)-2-(1-propynyl)isothiourea 5.** Potassium *tert*-butoxide (0.11 g, 1 mmol) was added to a solution of 5-chloro-2-propargylthiopyrimidine (0.18 g, 1 mmol) in *tert*-butanol (10 ml). The mixture was stirred at room temperature for 2 h, neutralized with acetic acid, water (30 ml) added and the mixture extracted with chloroform. The dried (MgSO<sub>4</sub>) chloroform solution was evaporated and the residue purified on a silica gel column (chloroform); yield 0.18 g (89%), m.p. 182 °C. Anal. C<sub>7</sub>H<sub>7</sub>ClN<sub>2</sub>OS: C, H. <sup>1</sup>H NMR (CDCl<sub>3</sub>-acetone-*d*<sub>6</sub>): δ 2.40 (Me), 6.40 (s, 1 H), 8.20 (s, 1 H), 9.28 (CHO). IR (KBr): 3200 and 3100 (NH), 1660 cm<sup>-1</sup> (HC=O). MS[70 eV, *m/z* (% rel. int.)]: 204/202 (10/29, M), 185(9), 167(23), 140(10), 139(100), 114(12), 99(12), 72(19), 71(30).

**5-Chloro-2-propargylsulfinylpyrimidine 6a.** A mix-

ture of selenium dioxide (0.45 g, 4 mmol) and 35 % hydrogen peroxide (0.40 g, 4 mmol) in water (2.5 ml) was added to a solution of 5-chloro-2-propargylthiopyrimidine (0.78 g, 4 mmol) in methanol (10 ml). The mixture was stirred at room temperature for 18 h before water (50 ml) saturated with sodium chloride was added, and the mixture was subsequently extracted with chloroform (3 × 20 ml). The dried (MgSO<sub>4</sub>) chloroform solution was evaporated and the residue recrystallized from chloroform–light petroleum; yield 0.50 g (63 %), m.p. 92 °C. Anal. C<sub>7</sub>H<sub>5</sub>ClN<sub>2</sub>O<sub>2</sub>S: C, H. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.28 (HC≡, t, J 2 Hz), 3.87 and 4.09 (–CH<sub>2</sub>–SO, J 15 Hz), 8.85 (H-4, H-6), IR (KBr): 3235 (HC≡), 2110 and 2100 cm<sup>-1</sup> (–C≡C–). MS[70 eV, m/z (% rel. int.)]: 200 (13, M), 199(19), 173(33), 171(100), 146(25), 114(30), 113(31), 111(47).

**2-Allylsulfinyl-5-chloropyrimidine 6b.** 30 % Hydrogen peroxide (5.67 g, 50 mmol) was added to a solution of 2-allylthio-5-chloropyrimidine (1.87 g, 10 mmol) in acetic acid (15 ml) and the mixture stirred at room temperature for 24 h. The solution was concentrated at reduced pressure to a small volume, water (20 ml) added and the mixture extracted with chloroform. The chloroform solution was washed with aqueous K<sub>2</sub>CO<sub>3</sub>, the dried (MgSO<sub>4</sub>) solution evaporated and the residue recrystallized from chloroform–light petroleum; yield 1.60 g (78 %), m.p. 82 °C. Anal. C<sub>7</sub>H<sub>7</sub>ClN<sub>2</sub>O<sub>2</sub>S: C, H. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.7–4.0 (CH<sub>2</sub>–SO), 5.0–6.2 (vinyl), 8.86 (H-4, H-6). IR (KBr): 1550 (pyrimidine) 1060 cm<sup>-1</sup> (SO). MS[70 eV, m/z (% rel. int.)]: 204/202 (2/5, M), 185(8), 171(4), 114(6), 41(100).

**5-Chloro-2-propargylsulfonylpyrimidine 7a.** A mixture of 5-chloro-2-propargylthiopyrimidine (0.35 g, 1.9 mmol) and 90 % *m*-chloroperbenzoic acid (0.94 g, 4.9 mmol) in chloroform (20 ml) was stirred together at room temperature for 24 h before chloroform (20 ml) was added and the solution washed with 1 M NaHCO<sub>3</sub> (2 × 30 ml). The dried (MgSO<sub>4</sub>) chloroform solution was evaporated and the residue recrystallized from methanol–water; yield 0.30 g (73 %), m.p. 70 °C. Anal. C<sub>7</sub>H<sub>5</sub>ClN<sub>2</sub>O<sub>2</sub>S: C, H. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.36 (HC≡, t, J 2 Hz), 4.39 (CH<sub>2</sub>–SO<sub>2</sub>, d, J 2 Hz) 8.78 (H-4, H-6). IR (KBr): 3270 (HC≡), 1320 and 1120 cm<sup>-1</sup> (SO<sub>2</sub>). MS[70 eV, m/z (% rel. int.)]: 218/216 (4/10, M), 154 (16), 152(52), 127(15), 125(46), 117(38), 115(26), 114(15), 113(78), 90(28), 88(16), 86(45).

**2-Allylsulfonyl-5-chloropyrimidine 7b.** 90 % *m*-Chloroperbenzoic acid (1.14 g, 6 mmol) was added to a solution of 2-allylthio-5-chloropyrimidine (0.43 g, 2.3 mmol) in chloroform (10 ml) and the mixture stirred at 40 °C for 90 min. The cold reaction mixture was extracted with aqueous K<sub>2</sub>CO<sub>3</sub>, the chloroform solution dried (MgSO<sub>4</sub>), the solution evaporated and the residue recrystallized from

methanol; yield 0.35 g (70 %), m.p. 84 °C. Anal. C<sub>7</sub>H<sub>7</sub>ClN<sub>2</sub>O<sub>2</sub>S: C, H. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.24 (CH<sub>2</sub>, J 7 Hz) 5.1–6.2 (vinyl), 8.90 (H-4, H-6). IR (KBr): 1550 (pyrimidine), 1330 and 1140 cm<sup>-1</sup> (SO<sub>2</sub>). MS[70 eV, m/z (% rel. int.)]: 155(30), 154(9), 153(82), 128(11), 113(9), 86(12), 53(17), 41(100).

**5-Chloro-2-propadienylsulfonylpyrimidine 7c.**

**Method A.** A mixture of 5-chloro-2-propadienylthiopyrimidine (0.21 g, 1.1 mmol) and 90 % *m*-chloroperbenzoic acid (0.49 g, 2.6 mmol) in chloroform was stirred together at room temperature for 24 h before washing with aqueous K<sub>2</sub>CO<sub>3</sub>. The dried (MgSO<sub>4</sub>) chloroform solution was evaporated and the residue recrystallized from methanol; yield 0.22 g (92 %), m.p. 130 °C. Anal. C<sub>7</sub>H<sub>5</sub>ClN<sub>2</sub>O<sub>2</sub>S: C, H. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ 5.65 (H<sub>2</sub>C d, J 6 Hz), 6.73 (=CH–SO<sub>2</sub>, t, J 6 Hz), 9.04 (H-4, H-6). IR (KBr): 1960 and 1920 (allene), 1550 (pyrimidine), 1330 and 1140 cm<sup>-1</sup> (SO<sub>2</sub>). MS[70 eV, m/z (% rel. int.)]: 218/216 (3/7, M), 152(26), 125(29), 113(52), 86(39), 53(45), 39(100).

**Method B.** A mixture of 5-chloro-2-propargylthiopyrimidine (0.39 g, 1.9 mmol) and 90 % *m*-chloroperbenzoic acid (0.94 g, 4.9 mmol) was stirred together in chloroform (20 ml) at room temperature for 24 h before chloroform (10 ml) was added and the solution washed with saturated K<sub>2</sub>CO<sub>3</sub> (2 × 20 ml). The dried (MgSO<sub>4</sub>) chloroform solution was evaporated and the residue recrystallized from methanol; yield 0.27 g (66 %).

**5-Chloro-2-(3-oxobuten-1-yl)sulfonylpyrimidine 7d** 90 % *m*-Chloroperbenzoic acid (2.20 g, 11.5 mmol) in chloroform (10 ml) was added to a solution of 5-chloro-2-(3-oxobuten-1-yl)thiopyrimidine (1.10 g, 5 mmol) in chloroform (10 ml) and the mixture stirred at 40 °C for 2 h. The cold reaction mixture was extracted with aqueous KHCO<sub>3</sub> and the dried (MgSO<sub>4</sub>) chloroform solution evaporated; yield 1.14 g (92 %). The (*E*)/(*Z*) isomers could be separated by thick layer chromatography [silica gel; CHCl<sub>3</sub>: EtOA (1:1)]. (*E*): m.p. 117 °C (MeOH). Anal. C<sub>8</sub>H<sub>7</sub>ClN<sub>2</sub>O<sub>3</sub>S: C, H. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ 2.43 (Me), 7.12 and 7.68 (H<sub>α</sub>, H<sub>β</sub>, d, J 16 Hz), 9.10 (H-4, H-6). IR (KBr): 1695 (CO), 1330 and 1140 cm<sup>-1</sup> (SO<sub>2</sub>). MS[70 eV, m/z (% rel. int.)]: 246 (5, M), 231(5), 203(40), 182(41), 167(32), 161(50), 114(100). (*Z*): m.p. 95 °C (MeOH). Anal. C<sub>8</sub>H<sub>7</sub>ClN<sub>2</sub>O<sub>3</sub>S: C, H. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): δ 2.32 (Me), 6.97 and 7.13 (H<sub>α</sub>, H<sub>β</sub>, d, J 12 Hz), 9.10 (H-4, H-6). IR (KBr): 1700 (CO), 1320 and 1140 cm<sup>-1</sup> (SO<sub>2</sub>). MS[70 eV, m/z (% rel. int.)]: 246(17), M), 231(40), 203(14), 182(38), 167(94), 161(75), 114(100).

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