

## 4-(SUBSTITUTED) BENZYLTHIOSEMICARBAZONES

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4-Substituted benzylthiosemicarbazones have been prepared by the action of 4-(substituted) benzylthiosemicarbazides on aryl aldehydes.

Following the discovery of the tuberculostatic activity of *p*-acetamidobenzaldehyde thiosemicarbazone by Dornagk *et al.* (*Naturwiss.*, 1946, **33**, 315) a large number of thiosemicarbazones of aryl and hetero aldehydes and ketones have been prepared. 4-Chloro- and 4-bromo-benzylthioureas have been reported to show tuberculostatic activity (Mrs. Shah, Ph. D. thesis, Bombay Univ., 1957). This observation prompted us to prepare thiosemicarbazones containing a substituted benzyl group. 4-(Substituted) benzylthiosemicarbazones have been prepared by the condensation of 4-(substituted) benzylthiosemicarbazides with aromatic aldehydes.

### EXPERIMENTAL

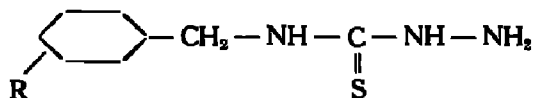
4-(Substituted) benzylthiosemicarbazides were prepared by the action of benzyl isothiocyanates (Trivedi *et al.*, this *Journal*, 1956, **33**, 423; 1958, **35**, 658) on hydrazine hydrate in cold (Buu Hoi *et al.*, *J. Chem. Soc.*, 1956, 2160).

4-(Substituted) benzylthiosemicarbazones were prepared by the action of 4-(substituted) benzylthiosemicarbazides on aromatic aldehydes in ethanolic solution (Buu Hoi *et al.*, *loc. cit.*).

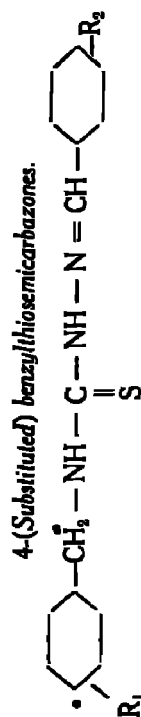
All the compounds were crystallised from dilute ethanol.

TABLE I

#### 4-(Substituted) benzylthiosemicarbazides.



No.	R.	M.P.	Formula.	% Sulphur.	
				Found.	Calc.
1.	<i>o</i> -Chloro	141°	C <sub>9</sub> H <sub>10</sub> N <sub>3</sub> ClS	15.0	14.9
2.	<i>p</i> -Chloro	156°	C <sub>9</sub> H <sub>10</sub> N <sub>3</sub> ClS	14.9	14.9
3.	<i>p</i> -Bromo	135°	C <sub>9</sub> H <sub>10</sub> N <sub>3</sub> BrS	12.4	12.3
4.	<i>o</i> -Methyl	152°	C <sub>9</sub> H <sub>12</sub> N <sub>3</sub> S	16.3	16.4
5.	<i>m</i> -Methyl	106°	C <sub>9</sub> H <sub>12</sub> N <sub>3</sub> S	16.3	16.4
6.	<i>p</i> -Methyl	156°	C <sub>9</sub> H <sub>12</sub> N <sub>3</sub> S	16.5	16.4
7.	2: 4-Dimethyl	129°	C <sub>10</sub> H <sub>14</sub> N <sub>3</sub> S	15.2	15.3
8.	3: 4-Dimethyl	176°	C <sub>10</sub> H <sub>14</sub> N <sub>3</sub> S	15.4	15.3
9.	2: 5-Dimethyl	181°	C <sub>10</sub> H <sub>14</sub> N <sub>3</sub> S	15.4	15.3

TABLE II  
4-(Substituted) benzylthiosemicarbazones.

R <sub>1</sub>	M.P.	Formula.	% Sulphur.		M.P.	Formula.	% Sulphur.		M.P.	Formula.	% Sulphur.	
			Found.	Calc.			Found.	Calc.			Found.	Calc.
H	178°	C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> ClS	10.6	10.5	151°	C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> ClS	10.5	10.5	138°	C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> BrS	9.1	9.2
	199°	C <sub>18</sub> H <sub>14</sub> ON <sub>4</sub> ClS	10.1	10.0	192°	C <sub>18</sub> H <sub>14</sub> ON <sub>4</sub> ClS	10.0	10.0	185°	C <sub>18</sub> H <sub>14</sub> ON <sub>4</sub> SBr	8.8	8.8
p-OMe	168°	C <sub>18</sub> H <sub>16</sub> ON <sub>4</sub> ClS	9.6	9.6	170°	C <sub>18</sub> H <sub>16</sub> ON <sub>4</sub> ClS	9.7	9.6	129°	C <sub>18</sub> H <sub>16</sub> ON <sub>4</sub> BrS	8.6	8.5
o-Cl	195°	C <sub>18</sub> H <sub>13</sub> N <sub>4</sub> Cl <sub>2</sub>	9.6	9.5	145°	C <sub>18</sub> H <sub>13</sub> N <sub>4</sub> Cl <sub>2</sub> S	9.5	9.5	147°	C <sub>18</sub> H <sub>13</sub> N <sub>4</sub> BrClS	8.5	8.4
p-Cl	184°	C <sub>18</sub> H <sub>15</sub> N <sub>4</sub> Cl <sub>2</sub> S	9.5	9.5	165°	C <sub>18</sub> H <sub>15</sub> N <sub>4</sub> Cl <sub>2</sub> S	9.6	9.5	151°	C <sub>18</sub> H <sub>15</sub> N <sub>4</sub> BrClS	8.5	8.4
2:4-Cl <sub>2</sub>	209°	C <sub>18</sub> H <sub>13</sub> N <sub>4</sub> Cl <sub>2</sub> S	8.7	8.6	175°	C <sub>18</sub> H <sub>13</sub> N <sub>4</sub> Cl <sub>2</sub> S	8.7	8.6	185°	C <sub>18</sub> H <sub>13</sub> N <sub>4</sub> BrCl <sub>2</sub> S	7.8	7.7
p-OH	220°	C <sub>18</sub> H <sub>16</sub> ON <sub>4</sub> ClS	10.0	10.0	220°	C <sub>18</sub> H <sub>16</sub> ON <sub>4</sub> ClS	10.0	10.0	209°	C <sub>18</sub> H <sub>16</sub> ON <sub>4</sub> BrS	8.9	8.8
p-(CH <sub>3</sub> ) <sub>2</sub> N	166°	C <sub>17</sub> H <sub>14</sub> N <sub>4</sub> ClS	9.3	9.2	174°	C <sub>17</sub> H <sub>14</sub> N <sub>4</sub> ClS	9.3	9.2	162°	C <sub>17</sub> H <sub>14</sub> N <sub>4</sub> BrS	8.3	8.2
			R <sub>1</sub> = o-Me.						R <sub>1</sub> = p-Me.			
H	132°	C <sub>18</sub> H <sub>17</sub> N <sub>4</sub> S	11.4	11.3	113°	C <sub>18</sub> H <sub>17</sub> N <sub>4</sub> S	11.4	11.3	132°	C <sub>18</sub> H <sub>17</sub> N <sub>4</sub> S	11.4	11.3
o-OH	181°	C <sub>18</sub> H <sub>17</sub> ON <sub>4</sub> S	10.7	10.7	152°	C <sub>18</sub> H <sub>17</sub> ON <sub>4</sub> S	10.7	10.7	201°	C <sub>18</sub> H <sub>17</sub> ON <sub>4</sub> S	10.7	10.7
p-OMe	150°	C <sub>17</sub> H <sub>15</sub> ON <sub>4</sub> S	10.2	10.2	166°	C <sub>17</sub> H <sub>15</sub> ON <sub>4</sub> S	10.3	10.2	168°	C <sub>17</sub> H <sub>15</sub> ON <sub>4</sub> S	10.3	10.2
o-Cl	178°	C <sub>18</sub> H <sub>16</sub> N <sub>4</sub> ClS	10.2	10.1	155°	C <sub>18</sub> H <sub>16</sub> N <sub>4</sub> ClS	10.2	10.1	172°	C <sub>18</sub> H <sub>16</sub> N <sub>4</sub> ClS	10.2	10.1
p-Cl	175°	C <sub>18</sub> H <sub>16</sub> N <sub>4</sub> ClS	10.1	10.1	158°	C <sub>18</sub> H <sub>16</sub> N <sub>4</sub> ClS	10.1	10.1	179°	C <sub>18</sub> H <sub>16</sub> N <sub>4</sub> ClS	10.1	10.1
2:4-Cl <sub>2</sub>	209°	C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> Cl <sub>2</sub> S	9.2	9.1	166°	C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> Cl <sub>2</sub> S	9.2	9.1	177°	C <sub>18</sub> H <sub>14</sub> N <sub>4</sub> Cl <sub>2</sub> S	9.2	9.1
p-OH	196°	C <sub>18</sub> H <sub>17</sub> ON <sub>4</sub> S	10.8	10.7	162°	C <sub>18</sub> H <sub>17</sub> ON <sub>4</sub> S	10.8	10.7	215°	C <sub>18</sub> H <sub>17</sub> ON <sub>4</sub> S	10.8	10.7
p-(CH <sub>3</sub> ) <sub>2</sub> N	149°	C <sub>17</sub> H <sub>15</sub> N <sub>4</sub> S	9.8	9.8	105°	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> S	9.9	9.8	150°	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> S	9.7	9.8

TABLE II—*contd.*

R <sub>2</sub>	Formula.	M.P.	% Sulphur.		M.P.	% Sulphur.		M.P.	% Sulphur.	
			Found.	Calc.		Found.	Calc.		Found.	Calc.
			R <sub>1</sub> = 3:4-Dimethyl.		R <sub>1</sub> = 2:4-Dimethyl.		R <sub>1</sub> = 2:5-Dimethyl.			
H	C <sub>17</sub> H <sub>19</sub> N <sub>3</sub> S	121°	10.7	10.8	182°	10.9	10.8	125°	10.9	10.8
<i>o</i> -OH	C <sub>17</sub> H <sub>19</sub> ON <sub>3</sub> S	171°	10.3	10.2	207°	10.3	10.2	201°	10.3	10.2
<i>p</i> -OMe	C <sub>18</sub> H <sub>21</sub> ON <sub>3</sub> S	142°	9.8	9.8	161°	9.9	9.8	141	9.8	9.8
<i>o</i> -Cl	C <sub>17</sub> H <sub>18</sub> N <sub>3</sub> ClS	184°	9.8	9.7	150°	9.7	9.7	184	9.8	9.7
<i>p</i> -Cl	C <sub>17</sub> H <sub>18</sub> N <sub>3</sub> ClS	143°	9.8	9.7	188°	9.8	9.7	175	9.7	9.7
2,4-Cl <sub>2</sub>	C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> Cl <sub>2</sub> S	185°	8.8	8.7	208°	8.8	8.7	200°	8.8	8.7
<i>p</i> -OH	C <sub>17</sub> H <sub>19</sub> ON <sub>3</sub> S	164°	10.2	10.2	205	10.3	10.2	206	10.2	10.2
<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> N	C <sub>18</sub> H <sub>21</sub> N <sub>4</sub> S	175°	9.5	9.4	175°	9.5	9.4	146	9.5	9.4

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