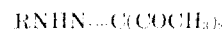
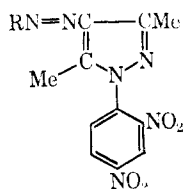


TABLE I

1-(2,4-DINITROPHENYL)-3,5-DIMETHYL-4-(SUBSTITUTED ARYLAZO)PYRAZOLES AND 2,3,4-PENTANETHIONE 3-ARYLHYDRAZONES



No.	R	Mp, °C	Color	Formula <sup>b</sup>	Mp, °C	Color	Formula <sup>c</sup>
1	Phenyl	259-260	Dark red	C <sub>17</sub> H <sub>14</sub> N <sub>6</sub> O <sub>4</sub>	84-85 <sup>a</sup>	Bright yellow needles	
2	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	216-218	Dull red	C <sub>17</sub> H <sub>13</sub> N <sub>7</sub> O <sub>6</sub>	173 <sup>a</sup>	Yellow plates	
3	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	236-237	Orange	C <sub>17</sub> H <sub>13</sub> N <sub>7</sub> O <sub>6</sub>	131 <sup>a</sup>	Golden yellow plates	
4	3-ClC <sub>6</sub> H <sub>4</sub>	257	Dark red	C <sub>17</sub> H <sub>13</sub> ClN <sub>6</sub> O <sub>4</sub>	78-79 <sup>a</sup>	Reddish yellow plates	
5	4-ClC <sub>6</sub> H <sub>4</sub>	254-255	Dark red	C <sub>17</sub> H <sub>13</sub> ClN <sub>6</sub> O <sub>4</sub>	129 <sup>a</sup>	Yellow needles	
6	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	252	Red	C <sub>18</sub> H <sub>16</sub> N <sub>6</sub> O <sub>4</sub>	90-91 <sup>a</sup>	Yellow needles	
7	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Above 300	Dark brown	C <sub>18</sub> H <sub>16</sub> N <sub>6</sub> O <sub>5</sub>	135	Yellow needles	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>
8	3-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Above 300	Orange	C <sub>18</sub> H <sub>16</sub> N <sub>6</sub> O <sub>5</sub>	76	Reddish yellow needles	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>
9	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	242-243	Brown	C <sub>18</sub> H <sub>16</sub> N <sub>6</sub> O <sub>5</sub>	95 <sup>a</sup>	Yellow needles	
10	2-C <sub>2</sub> H <sub>5</sub> OC <sub>6</sub> H <sub>4</sub>	260-262	Purple	C <sub>19</sub> H <sub>18</sub> N <sub>6</sub> O <sub>5</sub>	128	Bright yellow needles	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>
11	3-C <sub>2</sub> H <sub>5</sub> OC <sub>6</sub> H <sub>4</sub>	130	Reddish yellow	C <sub>19</sub> H <sub>18</sub> N <sub>6</sub> O <sub>5</sub>	102	Yellow	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>
12	4-C <sub>2</sub> H <sub>5</sub> OC <sub>6</sub> H <sub>4</sub>	134-135	Reddish yellow	C <sub>19</sub> H <sub>18</sub> N <sub>6</sub> O <sub>5</sub>	118	Bright red needles	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>
13	2,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	213-214	Orange	C <sub>17</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>4</sub>	120	Light yellow needles	C <sub>11</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>
14	2,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	203	Yellowish orange	C <sub>19</sub> H <sub>18</sub> N <sub>6</sub> O <sub>4</sub>	103-104	Yellow needles	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>
15	2,5-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	236-238	Brownish red	C <sub>19</sub> H <sub>18</sub> N <sub>6</sub> O <sub>6</sub>	128-129	Golden yellow needles	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>
16	2,4-(O <sub>2</sub> N) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	255-257	Orange	C <sub>17</sub> H <sub>12</sub> N <sub>8</sub> O <sub>8</sub>	163-164	Yellow needles	C <sub>11</sub> H <sub>10</sub> N <sub>4</sub> O <sub>6</sub>
17	2-Cl-4-O <sub>2</sub> NC <sub>6</sub> H <sub>3</sub>	254-255	Orange	C <sub>17</sub> H <sub>12</sub> ClN <sub>7</sub> O <sub>6</sub>	180 <sup>a</sup>	Yellow plates	
18	4-H <sub>2</sub> NSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>				205	Yellow plates	C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub> S

<sup>a</sup> Reference 8 and other references cited therein. <sup>b</sup> All compounds were analyzed for N, and the analytical values were within  $\pm 0.4\%$  of the calculated values. <sup>c</sup> As in footnote b, except for **1-6, 9, 17**.

separated which were recrystallized either from EtOH, DMF or DMF-EtOH. They were almost insoluble in H<sub>2</sub>O and soluble in organic solvents. The substituted pyrazoles which were prepared are also summarized in Table I.

**Acknowledgments.**—The authors wish to thank Professor W. U. Malik, Head of the Chemistry Department, for providing the necessary facilities for this work and the C.S.I.R., New Delhi (India), for a junior research fellowship (held by P. P. S.).

## Potential Antidiabetics. II. 1-(2,4-Dinitrophenyl)-3-methyl-4-arylazo-2-pyrazolin-5-ones

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In order to examine their hypoglycemic activity a series of 1-(2,4-dinitrophenyl)-3,5-dimethyl-4-arylazopyrazoles has been reported in the previous communication.<sup>1</sup> The present report concerns the synthesis of 1-(2,4-dinitrophenyl)-3-methyl-4-arylazo-2-pyrazolin-5-ones.

(1) H. G. Garg and P. P. Singh, *J. Med. Chem.*, **11**, 1103 (1968).

## Experimental Section<sup>2</sup>

**Ethyl 2,3-dioxobutyrates 2-arylhydrazones** were prepared by coupling diazotized anilines with ethyl acetoacetate<sup>3</sup> by the method of Garg<sup>4</sup> and are summarized in Table I on the following page.

**1-(2,4-Dinitrophenyl)-3-methyl-4-arylazo-2-pyrazolin-5-ones.**—Ethyl 2,3-dioxobutyrates 2-arylhydrazone (0.002 mol) was dissolved in 20 ml of glacial AcOH. To it was added a hot saturated solution of 2,4-dinitrophenylhydrazine (DNP) (0.004 mol) in glacial AcOH (nearly 1 g of DNP in 15 ml of AcOH). The contents were refluxed for 1 hr. On cooling, shining crystals separated out which were recrystallized either from DMF or AcOH. These derivatives are insoluble in H<sub>2</sub>O, soluble in CHCl<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>N, and sparingly soluble in EtOH, C<sub>6</sub>H<sub>6</sub>, AcOH.

These colored substances on treatment with H<sub>2</sub>O followed by KOH solution give color changes. Similar results are obtained with piperidine.

The substituted pyrazoles which were prepared are also summarized in Table I on the following page.

**Acknowledgment.**—The authors wish to thank Professor W. U. Malik, Head of the Chemistry Department, for providing the necessary facilities for carrying out the work and the C.S.I.R., New Delhi (India), for a Junior Research Fellowship (held by P. P. S.).

(2) Melting points are uncorrected.

(3) Commercially available.

(4) H. G. Garg, Ph.D. Thesis, University of Agra, 1959.

TABLE I

ETHYL 2,3-DIOXOBUTYRATE 2-ARYLHYDRAZONES AND 1-(2,4-DINITROPHENYL)-3-METHYL-4-ARYLAZO-2-PYRAZOLIN-5-ONES

No.	R	Mp, °C	Color and form	Formula <sup>b</sup>	Mp, °C	Color and form	Formula <sup>b</sup>
1	Phenyl	75-76 <sup>a</sup>	Pale yellow crystals	C <sub>12</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>	216-217	Violet-red needles <sup>c</sup>	C <sub>16</sub> H <sub>12</sub> N <sub>6</sub> O <sub>5</sub>
2	2-Nitrophenyl	94-95 <sup>a</sup>	Yellow needles	C <sub>12</sub> H <sub>13</sub> N <sub>3</sub> O <sub>5</sub>	235-236	Red crystals	C <sub>16</sub> H <sub>11</sub> N <sub>7</sub> O <sub>7</sub>
3	3-Nitrophenyl	115-117 <sup>a</sup>	Yellow needles	C <sub>12</sub> H <sub>13</sub> N <sub>3</sub> O <sub>5</sub>	252-253	Orange	C <sub>16</sub> H <sub>11</sub> N <sub>7</sub> O <sub>7</sub>
4	4-Nitrophenyl	125 <sup>a</sup>	Yellow needles	C <sub>12</sub> H <sub>13</sub> N <sub>3</sub> O <sub>5</sub>	260-261	Orange-red needles	C <sub>16</sub> H <sub>11</sub> N <sub>7</sub> O <sub>7</sub>
5	3-Chlorophenyl	71 <sup>a</sup>	Lt yellow needles	C <sub>12</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub>	221	Orange-red needles	C <sub>16</sub> H <sub>11</sub> ClN <sub>6</sub> O <sub>5</sub>
6	4-Chlorophenyl	82 <sup>a</sup>	Canary yellow needles	C <sub>12</sub> H <sub>13</sub> ClN <sub>2</sub> O <sub>3</sub>	242	Orange-red needles	C <sub>16</sub> H <sub>11</sub> ClN <sub>6</sub> O <sub>5</sub>
7	2-Methylphenyl	45-46 <sup>a</sup>	Pale yellow needles	C <sub>13</sub> H <sub>15</sub> N <sub>2</sub> O <sub>3</sub>	215	Violet-red needles	C <sub>17</sub> H <sub>14</sub> N <sub>6</sub> O <sub>5</sub>
8	3-Methylphenyl	72 <sup>a</sup>	Yellow needles	C <sub>13</sub> H <sub>15</sub> N <sub>2</sub> O <sub>3</sub>	228-229	Orange	C <sub>17</sub> H <sub>14</sub> N <sub>6</sub> O <sub>3</sub>
9	4-Methylphenyl	75 <sup>a</sup>	Orange crystals	C <sub>13</sub> H <sub>15</sub> N <sub>2</sub> O <sub>3</sub>	238-239	Brown-red needles	C <sub>17</sub> H <sub>14</sub> N <sub>6</sub> O <sub>5</sub>
10	2-Methoxyphenyl	99-100 <sup>a</sup>	Red crystals	C <sub>13</sub> H <sub>15</sub> N <sub>2</sub> O <sub>4</sub>	210-211	Red needles	C <sub>17</sub> H <sub>14</sub> N <sub>6</sub> O <sub>6</sub>
11	3-Methoxyphenyl	69-78	Dull red crystals	C <sub>13</sub> H <sub>15</sub> N <sub>2</sub> O <sub>4</sub>	212-213	Orange-red crystals	C <sub>17</sub> H <sub>14</sub> N <sub>6</sub> O <sub>6</sub>
12	4-Methoxyphenyl	68 <sup>a</sup>	Yellow crystals	C <sub>13</sub> H <sub>15</sub> N <sub>2</sub> O <sub>4</sub>	218	Brown-red needles	C <sub>17</sub> H <sub>14</sub> N <sub>6</sub> O <sub>6</sub>
13	2-Ethoxyphenyl	104	Pale yellow needles	C <sub>14</sub> H <sub>17</sub> N <sub>2</sub> O <sub>4</sub>	209-210	Orange-red needles	C <sub>18</sub> H <sub>16</sub> N <sub>6</sub> O <sub>6</sub>
14	4-Ethoxyphenyl	88-89	Pale yellow needles	C <sub>14</sub> H <sub>17</sub> N <sub>2</sub> O <sub>4</sub>	219-220	Violet-red needles	C <sub>18</sub> H <sub>16</sub> N <sub>6</sub> O <sub>6</sub>
15	2,5-Dichlorophenyl	101 <sup>a</sup>	Lt yellow needles	C <sub>13</sub> H <sub>13</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>3</sub>	233	Orange needles	C <sub>16</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>5</sub>
16	2,5-Dimethylphenyl	76-77	Yellow needles	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub>	214	Red needles	C <sub>18</sub> H <sub>16</sub> N <sub>6</sub> O <sub>3</sub>
17	2,5-Dimethoxyphenyl	118-119	Brick red crystals	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>5</sub>	231	Red needles	C <sub>18</sub> H <sub>16</sub> N <sub>6</sub> O <sub>7</sub>
18	2,6-Dichlorophenyl	74	Yellow needles	C <sub>13</sub> H <sub>13</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>3</sub>	186-187	Red-orange	C <sub>16</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>6</sub> O <sub>5</sub>
19	2,4-Dimethylphenyl	120-121	Pale yellow needles	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub>	218-219	Red needles	C <sub>18</sub> H <sub>16</sub> N <sub>6</sub> O <sub>3</sub>
20	2-Chloro-4-nitrophenyl	111 <sup>a</sup>	Yellow needles	C <sub>12</sub> H <sub>12</sub> ClN <sub>3</sub> O <sub>5</sub>	226-229	Orange needles	C <sub>16</sub> H <sub>10</sub> ClN <sub>7</sub> O <sub>7</sub>
21	4-Sulfanilamidophenyl	133-134	Yellow-orange needles	C <sub>12</sub> H <sub>13</sub> N <sub>3</sub> O <sub>5</sub> S	291-292	Orange	C <sub>16</sub> H <sub>13</sub> N <sub>7</sub> O <sub>5</sub> S

<sup>a</sup> Reference 4 and other references cited therein. <sup>b</sup> All the new compounds were analysed for N, and the analytical values were within  $\pm 0.4\%$  of the calculated values. <sup>c</sup> C. Bülow and A. Hecking, *Ber.*, **44**, 467 (1911).

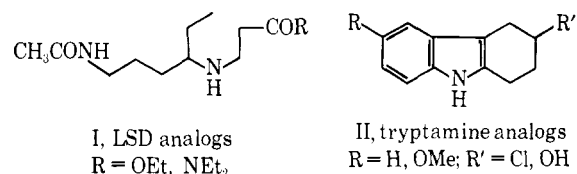
### Lysergic Acid Diethylamide (LSD) and Tryptamine Analogs as Potential Psychotomimetics

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We have been preparing analogs of hallucinogens and now report the synthesis of two series of analogs, one patterned after lysergic acid diethylamide (LSD) (I), and the other (II) after the tryptamine moiety found in many naturally occurring and synthetic hallucinogens.



Structures of compounds were confirmed by uv, ir, or nmr spectra.

Compounds in Table I, series I, were prepared by adding the appropriate amine to either ethyl acrylate or N,N-diethylacrylamide.<sup>1,2</sup> The tryptamine analogs (II) were prepared by the Borsche reaction,<sup>3</sup> except for 3-hydroxy-6-methoxy-1,2,3,4-tetrahydrocarbazole which was prepared from the corresponding 3-chloro compound, by prolonged pH 8-9 hydrolysis.

**4-Amino-N-acetylhexylamine.**—W-2 Raney nickel reduction of 4-nitro-N-acetylhexylamine gave the desired compound in 79% yield as a colorless oil, bp 131-133° (0.5 mm),  $n_D^{20}$  1.4742. *Anal.* (C<sub>8</sub>H<sub>18</sub>N<sub>2</sub>O) C, H, N.

TABLE I

Series I	Bp, °C (mm)	<i>n</i> <sub>D</sub> (t, °C)	Reaction time, days	Yield, %	Formula	Analyses
R = NEt <sub>2</sub> <sup>a</sup>	153 (0.5)	1.4765 (26)	4 <sup>b</sup>	55	C <sub>15</sub> H <sub>31</sub> N <sub>3</sub> O <sub>2</sub>	C, H, N
R = OEt <sup>c</sup>	190-192 (1.2)	1.4708 (23)	3 <sup>d</sup>	53	C <sub>13</sub> H <sub>26</sub> N <sub>2</sub> O <sub>3</sub>	C, H, N
Series II	Mp, °C	Recrystn solvent	Yield, %	Formula	Analyses	
R = OMe, R' = Cl <sup>e</sup>	157-160	Acetic acid	59	C <sub>13</sub> H <sub>14</sub> ClNO	C, H, Cl, N	
R = OMe, R' = OH	101-102	Water	30	C <sub>13</sub> H <sub>15</sub> NO <sub>2</sub>	C, H, N	
R = H, R' = Cl <sup>f</sup>	116-118	Acetic acid	56 <sup>g</sup>	C <sub>12</sub> H <sub>13</sub> ClN	C, H, N	

<sup>a</sup> From 4-amino-N-acetylhexylamine and N,N-diethylacrylamide. <sup>b</sup> At room temperature. <sup>c</sup> From 4-amino-N-acetylhexylamine and ethyl acrylate. <sup>d</sup> At room temperature under N<sub>2</sub>. <sup>e</sup> From 4-chlorocyclohexanone and 4-methoxyphenylhydrazine. <sup>f</sup> From phenylhydrazine and 4-chlorocyclohexanone, prepared according to R. Grewe, W. Lorenzen, L. Viving, *Chem. Ber.*, **87**, 797 (1954). The boiling point of the compound, the melting point of its semicarbazone, and the ir spectrum were confirmatory. <sup>g</sup> Semi-crude yield.

### Experimental Section

Where analyses are indicated only by symbols of the elements, analytical results obtained were within  $\pm 0.25\%$  of the theoretical values. Melting points were determined in capillary tubes in a melting point bath and, as with boiling points, are uncorrected. Microanalyses were performed by Galbraith Laboratories.

### 4-Nitro-N-acetylhexylamine.—Catalytic reduction of 4-nitro-

(1) P. E. Norris and F. F. Blicke, *J. Am. Pharm. Assoc., Sci. Ed.*, **41**, 637 (1952).

(2) G. H. Stempel, Jr., R. P. Gross, and R. P. Mariella, *J. Am. Chem. Soc.*, **72**, 2299 (1950).

(3) C. U. Robers and B. B. Corson, *ibid.*, **69**, 2910 (1947).