



TABLE I  
YIELDS AND PROPERTIES OF NORMAL ALIPHATIC 2,4-DIENALS, R-CH=CH-CH=CH-CHO

Empirical Formula	Yield, %	Boiling Point °C.	$n_D^4$	Specific Gravity	$\lambda_{max}$ , $\mu\mu$ (95% Ethanol)	$\epsilon_{max}$ (L./Mol. Cm.)	Carbon, %		Hydrogen, %	
							Calcd.	Found	Calcd.	Found
C <sub>5</sub> H <sub>6</sub> O	25	52-54.5 <sup>a</sup>	1.5110 <sup>25</sup>	0.885 <sup>25</sup>	258.5 325.0	27,800 51	73.14	71.8	7.37	7.4
C <sub>6</sub> H <sub>8</sub> O	57	68-68.5 <sup>b</sup>	1.5367 <sup>27</sup>	0.894 <sup>25</sup>	271.5	30,600	74.97	74.6	8.39	8.4
C <sub>7</sub> H <sub>10</sub> O	64	84-84.5 <sup>c</sup>	1.5313 <sup>27</sup>	0.881 <sup>25</sup>	272.5	32,500	76.32	76.4	9.15	9.2
C <sub>8</sub> H <sub>12</sub> O	77	83-85	1.5234 <sup>27</sup>	0.875 <sup>25</sup>	273.5	31,300	77.38	77.3	9.74	9.6
C <sub>9</sub> H <sub>14</sub> O	67	97-99 <sup>d</sup>	1.5184 <sup>27</sup>	0.862 <sup>25</sup>	274.0	30,100	78.21	77.8	10.21	10.1
C <sub>10</sub> H <sub>16</sub> O	54	114-116	1.5119 <sup>28</sup>	0.861 <sup>25</sup>	274.0	31,400	78.90	78.9	10.59	10.5
C <sub>11</sub> H <sub>18</sub> O	67	128-129 <sup>e</sup>	1.5102 <sup>28</sup>	0.857 <sup>25</sup>	274.0	32,600	79.45	79.3	10.92	10.8
C <sub>12</sub> H <sub>20</sub> O	61	136-137	1.5067 <sup>27</sup>	0.858 <sup>25</sup>	274.0	32,900	79.94	79.9	11.18	11.3

<sup>a</sup> 36-37 °C. (20 mm.), <sup>b</sup> 62-65 °C. (14 mm.), <sup>c</sup> 58-60 °C. (5 mm.), <sup>d</sup> 72-74 °C. (3 mm.), <sup>e</sup> 80-81 °C. (1 mm.).<sup>f</sup>

TABLE II  
PROPERTIES OF THE NORMAL ALIPHATIC 2,4-DIENAL-2,4-DINITROPHENYLDRAZONES, R-CH=CH-CH=CH-NH-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>

Number of Carbon Atoms in the Aldehyde	2,4-Dinitrophenylhydrazone, Empirical Formula	Color and Crystalline Form	Melting Point, °C.	$\lambda_{max}$ $\mu\mu$ (Chloroform)	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
5	C <sub>11</sub> H <sub>16</sub> N <sub>4</sub> O <sub>4</sub>	Red lozenges	180-181 <sup>a</sup>	383.0	50.38	50.3	3.84	3.8	21.37	20.9
6	C <sub>12</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub>	Purple needles	194.5-195.5 <sup>b</sup>	390.0	52.17	52.2	4.38	4.4	20.28	20.3
7	C <sub>13</sub> H <sub>20</sub> N <sub>4</sub> O <sub>4</sub>	Purple needles	157-159 <sup>c</sup>	391.0	53.79	53.9	4.86	4.8	19.30	19.1
8	C <sub>14</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub>	Red-brown scales	154-156	391.0	55.26	55.5	5.30	5.3	18.41	18.0
9	C <sub>15</sub> H <sub>24</sub> N <sub>4</sub> O <sub>4</sub>	Red scales	138.5-141 <sup>d</sup>	392.0	56.59	56.6	5.70	5.6	17.60	17.4
10	C <sub>16</sub> H <sub>26</sub> N <sub>4</sub> O <sub>4</sub>	Red platelets	143.6-145 <sup>e</sup>	391.5	57.82	57.8	6.07	5.9	16.86	16.6
11	C <sub>17</sub> H <sub>28</sub> N <sub>4</sub> O <sub>4</sub>	Red blades	134.5-135.5 <sup>f</sup>	391.0	58.95	58.9	6.40	6.3	16.18	15.9
12	C <sub>18</sub> H <sub>30</sub> N <sub>4</sub> O <sub>4</sub>	Red needles	130-131	391.0	59.98	60.0	6.71	6.6	15.55	15.3

<sup>a</sup> 176-177 °C., <sup>b</sup> 185-186 °C., <sup>c</sup> 153-156 °C., <sup>d</sup> 160.5-162.5 °C. (Form I), 155-157 °C. (Form II), <sup>e</sup> 136-138 °C., <sup>f</sup> 142-144 °C., <sup>g</sup> 141-142 °C., <sup>h</sup> 133-134 °C., <sup>i</sup>

dienals.<sup>3</sup> Also, it was observed that the 2,4-dinitrophenylhydrazones of hexa-2,4-dienal and hepta-2,4-dienal, synthesized by an alternate route,<sup>6,8</sup> proved to be identical to corresponding derivatives obtained in the present study.

In contrast to existing methods<sup>6,11</sup> used for preparation of some 2,4-dienals, the method described here offers the following advantages: starting materials are commercially available, all steps may be carried out in one flask without isolation of intermediates, the product is easy to purify, yields are good, and the general applicability is firmly established.

#### EXPERIMENTAL

**Aldehydes.** The saturated normal aliphatic aldehydes required were obtained from commercial sources. All, except formaldehyde, were dried over anhydrous sodium sulfate and distilled through a 90-cm. fractionating column packed with glass helices.

**1-Methoxybut-1-en-3-yne.** The commercially available material,<sup>12</sup> freshly redistilled, was used.

**Ethyl bromide.** Commercially available material was dried over calcium chloride and redistilled.

**Tetrahydrofuran.** Commercially available tetrahydrofuran was freshly distilled from lithium aluminum hydride before each preparation. Tetrahydrofuran was permitted to stand in contact with lithium aluminum hydride for at least 16 hr. before distillation. Occasionally a batch of tetrahydrofuran required two treatments before it was suitable.

**Melting point determinations.** Melting points were determined on an electrically heated stage and are corrected. A procedure was adopted in which the sample was placed on the stage only after the latter had been preheated to within about 5° of the expected melting point. This procedure avoids decomposition and in some instances resulted in both a sharper and higher melting point.

**Deca-2,4-dienal.** (VI, R = C<sub>6</sub>H<sub>11</sub>). Since all preparations, except for pentadienal, were carried out in the same way, only one example will be given for the preparation of the C<sub>6</sub> to C<sub>12</sub> members of the series.

1-Methoxybut-1-en-3-yne, 26.2 g. (0.32 mole), dissolved in 175 ml. of tetrahydrofuran was added dropwise with stirring to a Grignard reagent prepared from 7.3 g. of magnesium and 32.8 g. of ethyl bromide in 200 ml. of tetrahydrofuran while the mixture was maintained at about 40°. After an additional hour of stirring at room temperature, the reaction flask was cooled and there was added over a 20-min. period a solution of 25 g. (0.25 mole) of hexanal dissolved

in 50 ml. of tetrahydrofuran. After 2 hr. of stirring at room temperature, the mixture was cooled and treated with 11.5 g. (0.25 mole) of absolute ethanol. Twenty minutes later, solid lithium aluminum hydride, 9.5 g. (0.25 mole) was added in small portions over a 20- to 30-min. interval. The mixture was stirred for 2 hr. at room temperature and permitted to stand overnight. It was then treated successively with ethyl acetate (12 ml.), water (56 ml.), and 4*N* sulfuric acid (280 ml.). The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the ether extracts were combined, washed once with 10% sodium carbonate solution, three times with water, and dried over sodium sulfate. Most of the solvent was distilled off through a Vigreux column at atmospheric pressure, but reduced pressure was employed to distill off final amounts of solvent. The residue was then fractionally distilled *in vacuo* through a column 90 cm. long by 10 mm. outside diameter packed with glass helices. After a small forerun, deca-2,4-dienal (20.4 g., 54% yield) boiling at 114–116° (10 mm.) was obtained.

**Pentadienal.** (VI, R = H). For preparation of this member of the series, formaldehyde was sublimed from dry paraformaldehyde by heating the latter in an oil bath at 200° and was swept into the reaction mixture with a stream of nitrogen as described by Gilman and Catlin.<sup>13</sup> When 0.25 mole of paraformaldehyde was used, 8.1 g. of material boiling at 49.5–56.5° (52 mm.),  $n_D^{25}$  1.4894, were obtained. This material, although obviously impure, doubtless consisted mostly of pentadienal, for it gave a red 2,4-dinitrophenylhydrazone, m.p. 178–180°, and the fraction showed maxima at 285 and 325 m $\mu$  in the ultraviolet spectrum. A purer product, b.p. 52–52.4°,  $n_D^{25}$  1.5110 was obtained by using only 0.25 mole of 1-methoxybut-1-en-3-yne and 0.4 mole of paraformaldehyde. This procedure apparently consumes all of the enzyne compound; hence it cannot contaminate the product. Details of the properties of this particular preparation of pentadienal and the 2,4-dinitrophenylhydrazone are shown in Tables I and II.

A sample of pentadienal which the authors prepared according to Woods and Sanders,<sup>4</sup> was observed to have the following properties: b.p. 53–54° (46 mm.);  $n_D^{24}$  1.5114;  $\lambda_{\max}$  at 258.5 and 325 m $\mu$ ; 2,4-dinitrophenylhydrazone, red, m.p. 179–181°,  $\lambda_{\max}$  384 m $\mu$ .

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(13) H. Gilman and W. E. Catlin, *Org. Syntheses*, Coll. Vol. I, 188, (1944).

(3) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 1854 (1954).

(4) G. F. Woods and H. Sanders, *J. Am. Chem. Soc.*, **68**, 2483 (1946).

(5) E. R. Blout and M. Fields, *J. Am. Chem. Soc.*, **70**, 189 (1948).

(6) D. A. Forss and N. C. Hancox, *Australian J. Chem.*, **9**, 420 (1956).

(7) D. A. Forss, E. G. Pont, and W. Stark, *J. Dairy Research (Australia)*, **22**, 345 (1955).

(8) E. L. Pippen, M. Nonaka, F. T. Jones, and F. Stitt, *Food Research*, **23**, 103 (1958).

(9) R. J. Stapf and B. F. Daubert, *J. Am. Oil Chem. Soc.*, **27**, 374 (1950).

(10) D. LeFort, *Bull. mens. inform., ITERG*, **7**, 383 (1953). See also *Chem. Abstr.*, 388\* (1954).

(11) G. Wittig and P. Hornberger, *Ann.*, **577**, 11 (1952); E. Mosettig, *Org. Reactions*, **VIII**, 253–254 (1954).

(12) Aldrich Chemical Co., 3747 North Booth St., Milwaukee 12, Wis.

### Metalation Reactions of Triphenylgermyllithium

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Reactions of triphenylgermyllithium already reported<sup>1</sup> have pointed out the versatility of this re-

(1) (a) H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 5740 (1955); (b) A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **76**, 77 (1954); (c) H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **77**, 4675 (1955).