$(2.5 \times 10^{-2} \text{ mole})$  of mesityleneboronic acid and 2.6 g.  $(2.5 \times 10^{-2} \text{ mole})$  of diethanolamine. The resulting mixture was refluxed in a Stark-Dean apparatus for 3 hr. after which time water was no longer evolved. The toluene solution was cooled and treated with 100 ml. of pentane. Upon the addition of pentane an oily phase separated which would not crystallize upon repeated cooling and scratching of the glass surface. A small portion of the oil was separated and found to be completely miscible with water.

In a similar experiment di-*n*-butyl mesityleneboronate and an equivalent quantity of diethanolamine were placed in a large quantity of toluene and the toluene slowly distilled. After removal of the final traces of solvent in vacuum the residue was dissolved in a small portion of ethanol and crystallization was attempted without success.

Although the diethanolamine ester of mesityleneboronic acid was probably produced in both of the experiments described above the isolation of this compound by the methods chosen was perhaps unsuccessful due to its innate instability. Normally diethanolamine esters of aryl boronic acids are easily crystallized high melting solids which allow easy isolation.

Preparation of pyridine mesityl borane. Lithium aluminum hydride (0.8 g.) was refluxed with 50 ml. of ether for 1 hr. in a nitrogen atmosphere. The solution was cooled to  $-80^{\circ}$ and 3 ml. of dry pyridine added. This solution was vigorously stirred under nitrogen as 5.2 g. (0.019 mole) of di-*n*-butyl mesityleneboronate dissolved in 15 ml. of ether was added dropwise at  $-80^{\circ}$  over 1-hr. period. Following the addition the reaction mixture was allowed to stir at  $-80^{\circ}$  for 0.5 hr. and was then warmed to 0°. At 0° 2 ml. of pyridine dissolved in 4 ml. of water was added. The solution was filtered and the solvent removed in vacuum. The crystalline solid residue was recrystallized from ether pentane to afford 3.1 g. (78% theory) of pyridine mesityl borane melting at 116–118°.

Anal. Calcd. for  $C_{14}H_{18}BN$ : C, 79.64; H, 8.59; B, 5.13. Found: C, 79.74; H, 8.74; B, 5.09.

The acid catalyzed cleavage of mesityleneboronic acid. Mesityleneboronic acid (1.0 g.) was refluxed with 20 ml. of 10% sulfuric acid for 2 hr. Mesitylene was observed in the reflux condenser immediately after mixing the reagents. The reaction mixture was cooled and extracted with pentane. The pentane extract was washed once with water, dried over magnesium sulfate, and the solvent removed in vacuum. The residual oil weighed 0.6 g. and was identified as mesitylene by its infrared spectrum.

Hydrolysis of di-n-butyl mesityleneboronate. Two grams (0.0073 mole) of di-n-butyl mesityleneboronate was stirred magnetically at room temperature with 20 ml. of 10% sodium hydroxide solution. After a reaction period of 0.5 hr. the mixture was extracted with ethyl ether and the aqueous layer acidified with dilute hydrochloric acid. Whereupon, 1.05 g. (88%) of mesityleneboronic acid m.p.  $140-145^{\circ}$  was obtained.

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## A Convenient Method for Synthesizing Normal Aliphatic 2,4-Dienals

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Recently Marshal and Whiting<sup>1</sup> prepared a number of p-methoxyphenylpolyenealdehydes and

(1) D. Marshal and M. C. Whiting, J. Chem. Soc., 4082 (1956).

one polyene aliphatic aldehyde. Their results suggested that a general preparation of 2,4-dienals can be based on the sequence of reactions shown below. We have found that these reactions proceed



smoothly and that the normal aliphatic 2,4-dienals (VI) are readily obtained.

One might expect the enol vinyl ether (IV), on treatment with acid, to give the aldehyde (V). However, during this step there is spontaneous dehydration and rearrangement of the double bonds and the 2,4-dienals (VI) are isolated. Similar behavior of certain enol vinyl ethers of type IV has been reported by Inhoffen, Bohlmann, and Rummert<sup>2</sup> and Marshal and Whiting.<sup>1</sup> If the reaction proceeds through the enolaldehyde (V), some dehydration involving carbon atoms 5 and 6 would probably occur giving rise to some 3,5-dienal. In this study there was no indication that these isomers were formed. Neither did the workers cited above report the formation of 3,5-dienal isomers.

Table I lists the yields and data as determined on freshly distilled normal aliphatic 2,4-dienals. The 8, 10, and 12 carbon aldehydes are reported here for the first time. The aldehydes were obtained as pale yellow-green liquids. About 80% or more of the aldehydes could be recovered on redistillation after several months of storage in the dark at  $-34^{\circ}$ ; hence they were reasonably stable under these conditions. However some change had occurred during this storage as was evident from an observed increase in specific gravity and occasional appearance of solid polymer. On exposure to air at room temperature, the aldehydes underwent a relatively rapid polymerization and developed odors suggestive of the nutty, fatty, stale, or rancid types.

Table II lists data observed for the 2,4-dinitrophenylhydrazones. These derivatives showed a tendency to crystallize in polymorphic forms. Melting points, color, and crystalline forms listed in Table II are for forms most commonly obtained. The analytical data and the ultraviolet spectral properties confirm that these are derivatives of 2,4-

<sup>(2)</sup> H. H. Inhoffen, F. Bohlmann, and G. Rummert, Ann., 569, 226 (1950).

vdrogen, %	Found	7.4	8.4	9.2	9.6	10.1	2 10.5 11.3 2 11.3		
Ĥ	Calcd	7.37	8.39	9.15	9.74	10.21	10.59	10.92	11.18
24	Found	71.8	74.6	76.4	77.3	77.8	78.9	79.3	79.9
Carbon.	Jaled.	3.14	4.97	6.32	7.38	8.21	8.90	9.45	9.94
	() ()	2	2	2	2	2	7	2	2
	<sup>€max.</sup> (I/Mol. Cm.	27,800	30.600	32,500	31,300	30,100	31,400	32,600	32,900
	$^{\Lambda_{max., M}\mu}_{95\%}$ Ethanol)	258.5 325.0	271.5	272.5	273.5	274.0	274.0	274.0	274.0
	pecinc ravity (9	885*	89425	88125	87526	862*	86125	85726	$858^{26}$
Ű	n <sub>D</sub> t G	1.5110 <sup>25</sup> 0.	1.5367 <sup>27</sup> 0.	1.531327 0.	1.5234 <sup>27</sup> 0.	$1.5184^{27}$ 0.	1.511928 0.	$1.5102^{26}$ 0.	1.506727 0.
g Point	(Mm.)	(48)	(20)	( <b>50</b> )	(11)	(10)	(10)	(10)	(8)
Boilins	°C.	2-54.5ª	$3-68.5^{b}$	$1-84.5^{\circ}$	3-85	$p66^{-2}$	1116	$3-129^{e}$	3-137
Viold	1 menu, –	25 52	57 68	64 84	77 85	67 97	54 114	67 128	61 136
Emniriaal	Formula	C <sub>5</sub> H <sub>6</sub> O	C <sub>6</sub> H <sub>6</sub> O	$C_7H_{10}O$	C <sub>8</sub> H <sub>12</sub> O	C <sub>9</sub> H <sub>14</sub> O	C10H16O	$C_{11}H_{18}O$	$C_{12}H_{20}O$

# OCTOBER 1958

TABLE 1

<sup>a</sup> 176-177 °C, <sup>4 b</sup> 185-186 °C, <sup>7 c</sup> 153-156 °C, <sup>7</sup> 160,5-162,5 °C, (Form I), 155-157 °C, (Form II),<sup>8 d</sup> 136-138 °C, <sup>7 e</sup> 142-144 °C, <sup>7</sup> 141,2 °C, <sup>9</sup> 141-142 °C, <sup>10 f</sup> 133-134 °C, <sup>7</sup>

dienals.<sup>8</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>13</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,  $R = C_5H_{11}$ ). Since all preparations, except for pentadienal, were carried out in the same way, only one example will be given for the preparation of the  $C_6$  to  $C_{12}$  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

(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. **VOL.** 23

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 4N 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 Vigreaux 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  $49.5-56.5^{\circ}$  (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°,  $n_{\rm D}^{25}$  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 mµ; 2,4-dinitrophenylhydrazone, red, m.p. 179-181°,  $\lambda_{\max}$  384 mµ.

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

## Metalation Reactions of Triphenylgermyllithium

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

<sup>(1) (</sup>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).