

pened to be among the earliest made in the development of the magnetically-stirred diaphragm-cell, and were possibly not of the standard of precision obtained later, it seemed worthwhile to make some further measurements in this region. The technique used was closely similar to that described in reference (3), and gave the results in Table II, where the  $\bar{D}$  values have been converted to  $D^0$  values by the use of equation (1a). The means of the four new measurements using initially 1 *N* potassium chloride solution, the three using initially 0.7 *N* solution and the two using initially 0.45 *N* solution are shown as filled circles in the figure. It is evident that the original measurements near the minimum were in error by two or three times the estimated experimental error of 0.2%. In consequence of this, the smooth curve drawn through the open circles was appreciably different in shape near the minimum from what it should have been. Hence the differential diffusion coefficients obtained from it and reported in reference (3) differ in some cases by nearly 1% from those reported by Gosting.<sup>1</sup> It would appear that in using the diaphragm-cell method especially great care should be taken in regions of rapid change of slope of the integral diffusion coefficient. With this reservation it is clear that the diaphragm-cell measurements agree very well with the new absolute data obtained by Gosting.

In conclusion it would perhaps be as well to mention that in calibrating diaphragm-cells with the use of Table I, it is unwise to use any solution below 0.1 *N* in concentration at the start of the experiment, as at lower concentrations the anomalous surface-transport effect<sup>3</sup> becomes prominent.

#### CHEMISTRY DEPARTMENT

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### Allyl Butyl Ethers<sup>1</sup>

By E. A. TALLEY, ANN S. HUNTER AND E. YANOVSKY

It has been suggested that in our work on allyl starch,<sup>2</sup> one of the butyl alcohols might serve as a reaction solvent. The obvious objection to the use of alcohols in this reaction is the formation of ethers at the expense of allyl halide used for the main reaction. When an attempt was made to separate the allyl butyl ethers by fractionation of the organic layer of the reaction, azeotropes of the ether and alcohol were obtained.<sup>3</sup> Since attempts to separate the two by extracting the butyl alcohols with water were unsuccessful, at least in the case of normal and isobutyl alcohols, it was deemed advisable to learn more about the properties of pure allyl butyl ethers. In the literature, only the allyl isobu-

tyl ether has been reported.<sup>4</sup> It was prepared by catalytic dehydration of a mixture of the two corresponding alcohols. The boiling point (108–110°) was the only property given. We have, therefore, prepared the four allyl butyl ethers and determined some of their properties.

#### Experimental

**Preparation and Properties of Allyl Butyl Ethers.**—All ethers were prepared in the same manner. One to one and a half moles of butyl alcohol in 200 to 300 cc. of xylene was placed in a 1-liter three-necked flask furnished with a condenser, a stirrer and a separatory funnel. An equimolar quantity of sodium was gradually added to the solution. After the entire amount of sodium had been added, the reaction slowed down somewhat owing to coating of alkoxide on the metal. At this point, the bath temperature was raised to about 115° and the stirrer was started. The sodium melted, and the reaction proceeded. After all the sodium had disappeared, the flask was cooled to room temperature, and an equimolar amount of allyl bromide was gradually added through the separatory funnel. When the entire amount of allyl bromide had been added, the bath temperature was raised to 110–115° and kept at this temperature for about five hours. If any blue color remained at this time, methanol was added until the blue color disappeared. The mixture was then washed with water, dried and distilled. The theoretical amounts of allyl bromide were used for convenience of procedure at the expense of better yields. Under the conditions of the experiments, the yields were about 25% for the allyl *t*-butyl ether, 40% for the ether of isobutyl alcohol and 60% for the ethers of normal and secondary butyl alcohols.

Table I gives the properties of the four ethers.

TABLE I  
PROPERTIES OF ALLYL BUTYL ETHERS

Butyl group	Allyl (by Wils), % (theory, 36.0%)	B.p., °C.	Mm.	$d_{20}^4$	$n_D^{20}$	Mole refraction Calcd. <sup>a</sup>	Found
Normal	36.0	117.8–118.0	763	0.7829	1.4057	35.87	35.80
Second-ary	36.0	107.1–107.4	762	.7792	1.4023	35.70	35.70
Iso	36.0	106.6–107.0	749	.7735	1.4008	35.90	35.85
Tertiary	36.1	99.2–100.0	760	.7770	1.4011	35.83	35.71

<sup>a</sup> A. I. Vogel, *J. Chem. Soc.*, 1842 (1948).

(4) A. Mailhe and F. de Godon, *Bull. soc. chim.*, [4] **27**, 328 (1920).

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RECEIVED MARCH 1, 1951

### Unsaturated Lactones. II. The Relationship Between Chemical Constitution and Absorption Spectra in a Group of Crotonolactones<sup>1</sup>

By F. W. SCHUELER AND CALVIN HANNA

In a previous report<sup>2</sup> we had occasion to discuss the relationship between chemical constitution and the ultraviolet absorption spectra in a group of unsaturated azlactone derivatives. In the present communication we have extended this discussion to include a series of crotonolactones which derive part of their interest from the close chemical and physical similarities that they hold with respect to the unsaturated azlactones.

Out of a group of twenty crotonolactones<sup>3</sup> synthesized during this investigation four were re-

(1) This work was aided by a grant from the U. S. Public Health Service.

(2) F. W. Schueler and S. C. Wang, *THIS JOURNAL*, **72**, 2220 (1950).

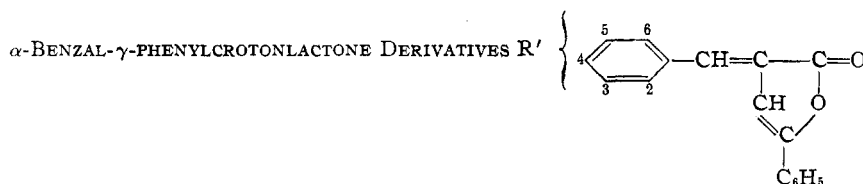
(3) These together with the azlactones and a group of related materials have been studied for cardiac activity and reported elsewhere. F. W. Schueler and C. Hanna, *Arch. Intern. Pharmacodyn. et Therapie*, in press, 1951.

(1) Contribution from one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) P. L. Nichols, Jr., R. M. Hamilton, Lee T. Smith and E. Yanovsky, *Ind. Eng. Chem.*, **37**, 201 (1945); E. A. Talley, R. M. Hamilton, J. H. Schwartz, C. A. Brown and E. Yanovsky, U. S. Dept. Agr., Bur. Agr. and Ind. Chem., AIC-140. (Eastern Regional Research Laboratory) Feb. 1947 (Processed).

(3) Cf. D. N. Kursanov and O. M. Shemyakina, *Doklady Akad. Nauk S. S. S. R.*, **62**, 341–343 (1948); C. A., **43**, 2159b (1949).

TABLE I



No.	R'	M.p., °C.	Formula	Analyses, %				Max. 1		Max. 2	
				Calcd.	Found	Calcd.	Found	$m\mu$	$\epsilon \times 10^4$	$m\mu$	$\epsilon \times 10^4$
1	2-NO <sub>2</sub> -	202	C <sub>17</sub> H <sub>11</sub> O <sub>4</sub> N	69.64	69.22	3.78	3.55	246	2.51	380	1.99
2	3-NO <sub>2</sub> - <sup>4</sup>	208						254	1.67	385	1.67
3	2,6-di-Cl-	170	C <sub>17</sub> H <sub>10</sub> O <sub>2</sub> Cl <sub>2</sub>	64.37	64.05	3.18	3.08	250	2.12	360	2.44
4	2-Cl-	164	C <sub>17</sub> H <sub>11</sub> O <sub>2</sub> Cl	72.22	71.99	3.92	3.73	252	2.12	388	2.52
5	3-CH <sub>3</sub> C-OO-	134	C <sub>19</sub> H <sub>13</sub> O <sub>4</sub>	74.74	74.17	4.29	4.11	250	1.44	388	1.98
6	No subs. <sup>5</sup>	155						250	1.87	384	2.97
7	2,3-di-CH <sub>3</sub> O- (o.) <sup>a</sup>	141	C <sub>19</sub> H <sub>16</sub> O <sub>4</sub>	74.01	74.36	5.23	5.75	252	2.53	389	3.43
8	4-CH <sub>3</sub> COO-	193	C <sub>19</sub> H <sub>18</sub> O <sub>4</sub>	74.74	74.52	4.29	4.20	252	2.10	395	3.07
9	4-CH <sub>3</sub> -	150	C <sub>18</sub> H <sub>17</sub> O <sub>2</sub>	82.42	82.81	6.54	6.72	250	1.82	393	3.49
10	4-iso-C <sub>3</sub> H <sub>7</sub> -	88	C <sub>20</sub> H <sub>18</sub> O <sub>2</sub>	82.73	82.58	6.25	6.46	250	1.74	400	2.86
11	4-CH <sub>3</sub> COO-3-CH <sub>3</sub> O- (o.) <sup>a</sup>	158	C <sub>20</sub> H <sub>16</sub> O <sub>6</sub>	71.42	71.15	4.80	4.86	253	2.72	394	3.87
12	3-Cl-4,5-di-CH <sub>3</sub> O-	160	C <sub>19</sub> H <sub>15</sub> O <sub>4</sub> Cl	66.43	66.51	4.41	4.17	255	2.78	400	4.57
13	4-CH <sub>3</sub> O- <sup>5</sup>	171						253	1.85	402	3.51
14	$\alpha$ -Furfural (br.) <sup>a,b</sup>	116	C <sub>15</sub> H <sub>10</sub> O <sub>4</sub>	75.62	75.25	4.23	4.02	259	1.78	405	3.81
15	4-NO <sub>2</sub> -	295	C <sub>17</sub> H <sub>11</sub> O <sub>4</sub> N	69.64	69.37	3.78	3.39	256	0.76	415	0.72
16	3,4-OCH <sub>2</sub> O-	177	C <sub>18</sub> H <sub>12</sub> O <sub>4</sub>	73.96	73.58	4.14	4.02	256	2.52	408	4.52
17	$\beta$ -Phenylvinyl <sup>5</sup> (o.) <sup>a,b</sup>	154						260	1.43	411	3.52
18	3,4-di-CH <sub>3</sub> CH <sub>2</sub> O-	128	C <sub>21</sub> H <sub>20</sub> O <sub>4</sub>	74.99	74.55	5.99	5.63	258	1.37	412	2.62
19	$\beta$ -Furylvinyl (br.) <sup>a,b</sup>	143-144.5	C <sub>17</sub> H <sub>12</sub> O <sub>3</sub>	77.26	77.43	4.58	4.69	259	0.50	424	1.77
20	4-(CH <sub>3</sub> ) <sub>2</sub> N- (r.) <sup>a</sup>	175	C <sub>19</sub> H <sub>17</sub> O <sub>2</sub> N	77.70	77.05	5.88	5.52	249	1.84	462	5.36

<sup>a</sup> All compounds had a yellow color except as otherwise noted, thus o. orange, r. red, br. brown. <sup>b</sup> These replace the benzal group.

corded in the literature and no spectroscopic data appear to have been reported on any of these materials. This is in direct contrast to the literature bearing upon the corresponding azlactones which have been widely investigated because of their importance as intermediates in the synthesis of amino acids, aryl acetic acids and many natural products. The crotonolactones synthesized in this study are detailed in Table I together with their absorption maxima, melting points and analysis.

A comparison of the colors and melting points of the crotonolactones with the azlactones of the previous study<sup>2</sup> reveals the fact that the parallel crotonolactones are uniformly more deeply tinted whereas the melting points hold no constant relationship. The color relationship is borne out by a study of the absorption spectra. Thus a comparison of the absorption maxima of the present series of crotonolactones with the parallel series of azlactones previously discussed<sup>2</sup> reveals that the crotonolactones are in general more bathochromic but otherwise exhibit a parallel behavior with regard to substitution. Curves illustrating the relationship between spectra in these series are given in Fig. 1.

#### Experimental

**Absorption Spectra.**—All spectra were determined with a Beckman quartz spectrophotometer, model DU, using ethanol as a solvent as outlined previously.<sup>2</sup>

**Preparation of Materials.**—The crotonolactones were prepared by the following general procedure: A mixture of 0.05 mole of the aldehyde, 0.05 mole of dry, powdered  $\beta$ -benzoylpropionic acid, 0.05 mole of freshly fused sodium acetate

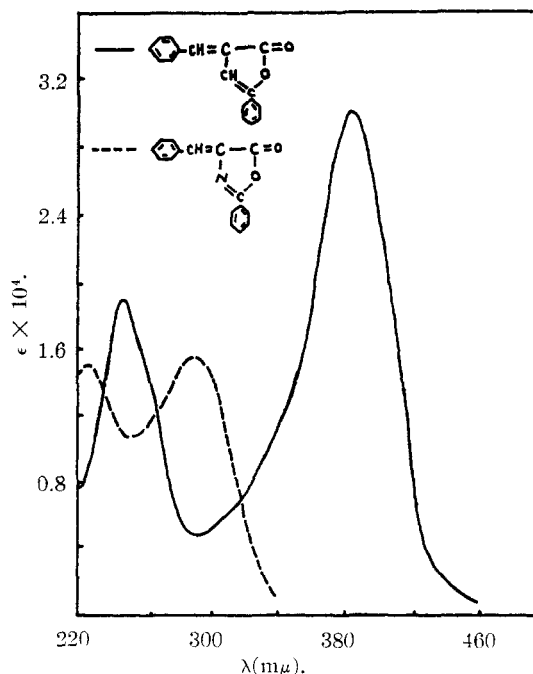


Fig. 1.—A comparison between the absorption curves of  $\alpha$ -benzal- $\gamma$ -phenylcrotonolactone (No. 6 of Table I) and the analogous azlactone, 2-phenyl-4-benzal-5-oxazolone.

and 16 ml. of acetic anhydride was heated in a beaker on a hot-plate until a complete solution was obtained. The beaker was then transferred to a steam-bath and heating was continued until crystals separated. The reaction was next poured into water, the solid product filtered with suction, washed with water and finally recrystallized repeatedly

(4) E. P. Kohler, G. A. Hill and L. A. Bigelow, *THIS JOURNAL*, **39**, 2417 (1917).

(5) W. Borsche, *Ber.*, **47**, 1108 (1914).

from 95% ethanol until a constant melting point was obtained. The yield, in general, ranged from 40–75%.

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### Preparation of Methyl 2,3,4-Triacetyl- $\alpha$ -D-xyloside<sup>1</sup>

BY ROY L. WHISTLER, K. ANN KIMMELL AND DONALD F. DURSO

During the course of work in this Laboratory it became necessary to prepare methyl 2,3,4-triacetyl- $\alpha$ -D-xylopyranoside in fairly large quantities. Direct preparation of this compound from D-xylose involves the preparation of pure methyl  $\alpha$ -D-xyloside and subsequent acetylation.<sup>2</sup> The procedure adopted in this work was to acetylate commercially available methyl  $\beta$ -D-xyloside to yield the corresponding triacetate,<sup>3</sup> from which the desired compound was easily prepared by isomerization with boron trifluoride using the procedure of Lindberg.<sup>4</sup> The yield of crystalline product was 85%.

#### Experimental

**Methyl 2,3,4-Triacetyl- $\beta$ -D-xyloside.**—Commercially available crystalline methyl  $\beta$ -D-xyloside (15.00 g.) was acetylated at 110° with sodium acetate and acetic anhydride. The acetate was isolated in the usual manner and recrystallized from 95% ethanol. The yield was 23.85 g. of material whose m.p. 114.5–115.5° and  $[\alpha]_D^{20}$  –61.2 (c, 2.42 in chloroform) agreed with the constants previously reported.<sup>3</sup>

*Anal.* Calcd. for  $C_6H_9O_5(CH_3CO)_3$ : acetyl, 44.49. Found: acetyl, 44.3.

**Methyl 2,3,4-Triacetyl- $\alpha$ -D-xyloside.**—The  $\beta$ -compound (5.00 g.) was dissolved in 150 ml. of dry chloroform and the solution saturated with  $BF_3$ . Saturation was indicated by the formation of a white gelatinous precipitate in 10 min. The flow of gas was interrupted and the reaction flask stoppered. After 24 hours, the solution was treated with two 100-ml. portions of saturated sodium bicarbonate solution followed by three 150-ml. washes with water. The chloroform solution was dried over anhydrous sodium sulfate. Upon removal of the chloroform the product crystallized spontaneously. The yield was 4.29 g. After recrystallization from 95% ethanol, m.p. was 86–87° and  $[\alpha]_D^{20}$  +120.1 (c, 1.59 in chloroform). These values agreed with those previously reported for the desired product.<sup>2</sup>

*Anal.* Calcd. for  $C_6H_9O_5(CH_3CO)_3$ : acetyl, 44.49. Found: acetyl, 44.4.

(1) Paper No. 528 of the Purdue Agricultural Experiment Station.

(2) C. S. Hudson and J. K. Dale, *THIS JOURNAL*, **40**, 997 (1918).

(3) J. K. Dale, *ibid.*, **37**, 2745 (1915).

(4) B. Lindberg, *Acta Chem. Scand.*, **2**, 426 (1948).

DEPARTMENT OF AGRICULTURAL CHEMISTRY  
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RECEIVED MARCH 12, 1951

### $\beta$ -Amyrin from *Chimaphila umbellata*<sup>1a</sup>

BY F. P. VEITCH, JR., AND PEARL ADAIR WELTON<sup>1b</sup>

During our investigation of the plant *Chimaphila umbellata* as a possible source of steroids having an oxygen function in the 11 or 12 position, a white crystalline material was isolated in 0.25% yield. From the physical constants of this compound and its derivatives (Table I) we have concluded that it

(1) (a) Obtained from S. B. Penick, New York. (b) Taken from a thesis submitted to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Master of Science.

is  $\beta$ -amyrin, a substance not previously reported as being present in this plant.

#### Experimental

Four kilograms of air dry *Chimaphila umbellata* was obtained in a finely divided state by the use of a Williams crusher, rollers, and a Wiley mill. The finely ground material was treated by essentially the same process as that described by Marker<sup>2</sup> for the isolation of sapogenins from plant sources. Upon concentration of the final ethereal extract and addition of acetone, about 20 g. of crude crystalline material precipitated. Purification of this material was effected by recrystallization from acetone followed by formation of the acetate which could be crystallized from ethyl acetate. Saponification of the acetate followed by crystallization of the regenerated compound from ethyl alcohol gave 8.5 g. of material (0.21% yield based on the weight of air-dry plant) having the following characteristics: m.p. 200°;  $[\alpha]_D^{20}$  +87.7° (in  $CHCl_3$ ).

*Anal.* Calcd. for  $C_{30}H_{50}O$ : C, 84.43; H, 11.82. Found: C, 84.47, 84.58; H, 12.00, 12.00.

The acetate, benzoate and *p*-nitrobenzoate of this compound were prepared according to standard procedures. The physical constants of these derivatives and their analyses are summarized in Table I.

TABLE I<sup>a</sup>

Compound	M.p., <sup>b</sup> °C.	$[\alpha]_D^{20d}$	Analyses, %			
			Found <sup>c</sup>		Calculated	
			Carbon	Hydrogen	Carbon	Hydrogen
$\beta$ -Amyrin	200	+87.7	84.47	12.00	84.43	11.82
Acetate	243	+80.66	82.02	11.22	82.00	11.18
Benzoate	232	.....	83.68	10.57	83.71	10.26
<i>p</i> -Nitrobenzoate	257	.....	.....	.....	.....	.....

<sup>a</sup> The values reported here are in agreement with the values reported by other workers: cf. L. C. King, *et al.*, *THIS JOURNAL* **65**, 1168 (1943); A. Vesterburg, *Ber.*, **23**, 3186 (1890); N. H. Cohen, *Rec. trav. chim.*, **28**, 391; G. L. Powers, and W. E. Powers, *Pharm. Assoc.*, **29**, 175 (1940). <sup>b</sup> All melting points were determined on a Fisher-Johns melting point block. <sup>c</sup> We are indebted to Mrs. Mary Aldridge for the micro analyses reported here. <sup>d</sup> All rotations are in chloroform.

Values of 411 and 443 g. were obtained by the Rast method of molecular weight determination on the isolated compound, and 423 g. by the saponification method of the acetate.

$\beta$ -Amyrin has a molecular weight of 426 g.

(2) R. Marker, *et al.*, *THIS JOURNAL*, **69**, 2167 (1947).

DEPARTMENT OF CHEMISTRY  
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RECEIVED MARCH 7, 1951

### The Melting Point and the Heat of Sublimation of Plutonium Trifluoride<sup>1</sup>

BY EDGAR F. WESTRUM, JR., AND JAMES C. WALLMANN

Careful measurements by an effusion technique of the equilibrium vapor pressures over plutonium trifluoride ( $PuF_3$ ) have been reported.<sup>2a,b</sup> The slight deviation from linearity of the  $\log p$  versus  $1/T$  plot was represented by these authors without a stated reason as two straight lines intersecting at  $1169 \pm 9^\circ$ , which temperature was interpreted as the melting point of plutonium trifluoride.

(1) Based on work reported in MB-IP 327, September 17, 1948, issued as Report UCRL-697 (May 19, 1950).

(2) (a) T. E. Phipps, G. W. Sears, R. L. Seifert and O. C. Simpson, *J. Chem. Phys.*, **18**, 713 (1950); (b) T. E. Phipps, G. W. Sears, R. L. Seifert, and O. C. Simpson, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 6.1a (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).