

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.¹ 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 effect³ becomes prominent.

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Allyl Butyl Ethers¹

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It has been suggested that in our work on allyl starch,² 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.³ 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.⁴ 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 Wigs), % (theory, 36.0%)	B. p., °C.	Mm.	d_{20}^4	n_D^{20}	Mole refraction Calcd. ^a	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

^a 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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Unsaturated Lactones. II. The Relationship Between Chemical Constitution and Absorption Spectra in a Group of Crotonolactones¹

BY F. W. SCHUELER AND CALVIN HANNA

In a previous report² 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 crotonolactones³ 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 Therap.*, 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).