

The identity of the compounds was established by infrared absorption data and by mixed melting points with authentic samples of the materials. The nature of the nitrogen containing products was not investigated.

NEW PRODUCT DEVELOPMENT LABORATORY
CHEMICAL DIVISION, GENERAL ELECTRIC CO.
PITTSFIELD, MASS.

The Ultraviolet Absorption Spectra of Some Terpene Hydrocarbons

BY ROBERT D. WALKER, JR., AND J. ERSKINE HAWKINS
RECEIVED DECEMBER 12, 1951

The use of ultraviolet absorption spectra in the chemistry of the terpenes was suggested about 1910 in a series of papers by Hantzsch¹ and Auwers.² These authors reported the ultraviolet absorption of a few terpenes but little interest was shown in the subject for a number of years. More recently there has been a renewal of interest in the ultraviolet absorption spectra of terpenes and several have been reported.³⁻⁵ A relatively limited number of terpenes have been thus investigated, however, and it has seemed desirable to report the ultraviolet absorption spectra of some hydrocarbon terpenes which were available.

Experimental

The quantity of each sample used was determined by transferring an amount to a weighed volumetric flask partially filled with isoöctane and then reweighing. The flask was then filled to the 10-ml. mark with isoöctane and the solution thoroughly mixed. Successive 1:10 dilutions were made by transferring 1-ml. samples to 10-ml. volumetric flasks which were partially filled with isoöctane and then filling to the mark. Appropriate dilutions were made to give maximum optical densities of 0.4-0.9.

The spectra were measured with a Beckman spectrophotometer, using spectroscopic grade isoöctane (Phillips Petroleum Company) both as solvent and as standard.

Myrcene.—Myrcene was prepared by pyrolysis of β -pinene in the vapor phase at 465°. The pyrolysate was fractionated at reduced pressure to obtain myrcene which had a refractive index, n_D^{25} of 1.4683. Simonsen⁷ gives for this compound n_D^{25} 1.4700.

Ocimene.—The sample used in this investigation was prepared by vapor phase thermal isomerization of α -pinene and subsequent fractionation.⁸ It had a refractive index n_D^{25} 1.4831. Enklaar⁹ reported for ocimene n_D^{25} 1.4857.

Alloöcimene.—This compound was prepared by liquid phase thermal isomerization of α -pinene¹⁰ and fractionation at reduced pressure. It had a refractive index n_D^{25} 1.5418 as compared to the value n_D^{25} 1.5446 reported by Simonsen⁷ for the pure compound.

Alloöcimene Dimer.—Alloöcimene dimer was recovered by fractional distillation at reduced pressure of the mixture resulting from the liquid phase thermal isomerization of α -pinene. The sample used in this investigation had a refractive index n_D^{25} 1.5180. Fuguitt and Hawkins¹⁰ found for this substance n_D^{25} 1.5171-82.

(1) A. Hantzsch, *J. Chem. Soc.*, **99**, 1267 (1911); *Ber.*, **45**, 553, 963, 1743 (1912).

(2) K. Auwers, *ibid.*, **44**, 3538 (1911).

(3) H. Booker, L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 1453 (1940).

(4) A. Smakula, *Angew. Chem.*, **47**, 657 (1934).

(5) R. B. Woodward, *THIS JOURNAL*, **64**, 72 (1942).

(6) L. A. Goldblatt and S. Palkin, *ibid.*, **63**, 3517 (1941).

(7) J. L. Simonsen, "The Terpenes," 2nd Ed., Cambridge University Press, 1947.

(8) J. E. Hawkins and H. G. Hunt, *THIS JOURNAL*, **73**, 5379 (1951).

(9) C. J. Enklaar, *Rec. trav. chim.*, **26**, 157 (1907).

(10) R. E. Fuguitt and J. E. Hawkins, *THIS JOURNAL*, **67**, 242 (1945).

Results and Discussion

In Fig. 1 is shown the ultraviolet absorption curve of myrcene: λ_{\max} 224.5 $m\mu$; ϵ_{\max} 15,350. Two very interesting subsidiary absorption bands appear as shoulders on the main absorption band with maxima at approximately 280 and 320 $m\mu$. The band at 280 $m\mu$ may most probably be attributed to the presence of a small amount of alloöcimene (see Fig. 2). This compound would result from the thermal isomerization of any trace of α -pinene remaining in the β -pinene from which the myrcene was prepared by pyrolysis.^{4,6} The substance responsible for the absorption at 320 $m\mu$ seems to be present in only trace quantities, and it does not now seem possible to attribute this absorption band to any known compound. It may be of some importance, however, to note that absorption in this region appears in the pyrolysis products of α - or β -pinene, but not in the absorption of the parent substances.

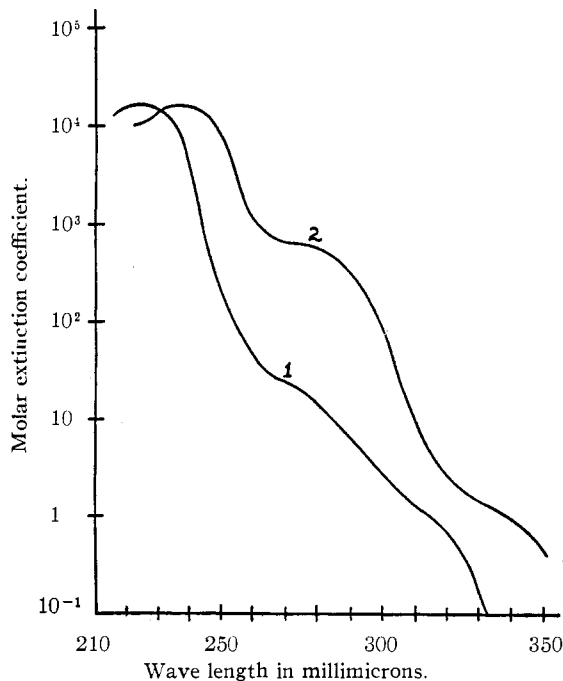


Fig. 1.—Ultraviolet absorption spectra in isoöctane at about 30°: 1, myrcene; 2, ocimene.

Also shown in Fig. 1 is the ultraviolet absorption of ocimene, 2,6-dimethyl- $\Delta^{1:5:7}$ -octatriene; λ_{\max} is 237 $m\mu$ and ϵ_{\max} 16,400. The presence of approximately 2% of alloöcimene is indicated by the very prominent subsidiary band at 270-280 $m\mu$. This can be accounted for by the relations between α -pinene, ocimene and alloöcimene.⁸ Traces of the constituent absorbing at 320 $m\mu$ are also noted as in myrcene.

The ultraviolet absorption of alloöcimene, 2,6-dimethyl- $\Delta^{2:4:6}$ -octatriene, is shown in Fig. 2. Alloöcimene shows three absorption peaks at 268, 277 and 288 $m\mu$, ϵ_{\max} being greatest (41,900) at 277 $m\mu$. On the short wave length side of the broad triply-peaked maximum of alloöcimene there appear several hindered transitions in the alloöcimene mole-

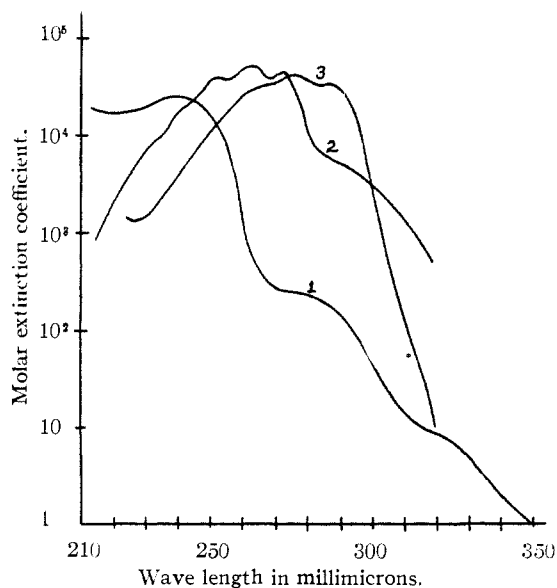


Fig. 2.—Ultraviolet absorption spectra in isoöctane at about 30°: 1, alloöcimene dimer; 2, 2,4,6-octatriene; 3, alloöcimene.

cule but it is equally possible that they are due to the presence of small amounts of ocimene and alloöcimene dimer, with which alloöcimene is in equilibrium.¹⁰

In the course of the literature search preceding this investigation it was noted that Blout and Fields¹¹ had measured the ultraviolet absorption of 2,4,6-octatriene. Through the courtesy of Dr. Blout these data, previously unpublished in complete form, were made available to the authors and are shown in Fig. 2. This compound has the same resonance system as alloöcimene and it is not surprising to find a marked similarity between the absorption curves. 2,4,6-Octatriene has absorption peaks at 253, 263 and 274 $m\mu$, the peak at 263 $m\mu$ being slightly higher than the other two. ϵ_{\max} at 263 $m\mu$ is 53,000. Each of the three main absorption bands in alloöcimene is thus shifted about 14 $m\mu$ toward longer wave lengths than in 2,4,6-octatriene.

Ultraviolet absorption data for alloöcimene dimer are shown in Fig. 2. The marked shift of the absorption peak from 277 to 240 $m\mu$ is indicative of a change from a triene to a diene chromophore as a result of dimerization. The spectral absorption curve clearly indicates the presence of a small amount of alloöcimene, most probably arising from depolymerization of the dimer,¹⁰ and traces of the substance absorbing at 320 $m\mu$.

Parker and Goldblatt¹² studied the thermal isomerization of alloöcimene in the vapor phase and reported that the products consisted almost entirely of cyclohexadienes having absorption maxima between 260–265 $m\mu$. An examination of Fig. 2 indicates that cyclohexadienes are not major products of the liquid phase thermal isomerization, although their absence cannot be positively demonstrated on the basis of the ultraviolet absorption spectra available.

(11) E. R. Blout and M. Fields, *THIS JOURNAL*, **70**, 189 (1948).

(12) E. D. Parker and L. A. Goldblatt, *ibid.*, **72**, 2151 (1950).

Values of λ_{\max} for myrcene, ocimene and alloöcimene dimer calculated by Woodward's⁵ method were compared with those observed experimentally. In the cases of ocimene and the alloöcimene dimer the values differ by more than the 5 $m\mu$ found by Woodward (see Table I).

TABLE I

Compound	λ_{\max} calcd., $m\mu$	λ_{\max} obsd., $m\mu$
Myrcene	222	224.5
Ocimene	227	237
Alloöcimene dimer	232	240

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA

Synthesis of α - and β -Lactose-1-phosphate^{1,2}

BY F. J. REITHEL AND R. G. YOUNG

RECEIVED MARCH 7, 1952

Lactose-1-phosphate has been postulated as an intermediate in lactose synthesis in mammary gland³ and has been suggested as an intermediate in lactose fermentation by yeasts.⁴ A preliminary examination of the behavior of this compound in mammary gland homogenates has been reported.⁵

The method of Cori,⁶ employing trisilver phosphate as a phosphorylating agent, was adapted to the preparation of α -lactose-1-phosphate, but yields were poor. The product obtained possessed constants approximating those reported in the experimental description following but an analytically pure product could not be prepared.

Similarly, attempts were made to use the procedures described by Posternak⁷ in which silver diphenyl phosphate was used as a phosphorylating agent. Again, yields were low and the product was difficult to purify. However, it was possible to introduce modifications which allowed the successful application of the principles of this latter procedure.

The use of monosilver phosphate for the preparation of β -isomers of the sugar phosphates⁸ was successfully applied to the preparation of β -lactose-1-phosphate.

Experimental

1-Bromoheptaacetyl- α -lactose.—To ensure purity of the final product it was found necessary to prepare a very pure starting material.

To 20 g. of pure octaacetylactose in a stoppered flask was added 50 ml. of 30% hydrogen bromide in glacial acetic acid. The mixture was shaken occasionally during a reaction period of 1.5–2 hours and then poured slowly into a liter of ice-water with efficient stirring. The precipitate was collected on a buchner funnel and pressed dry. The cake was dissolved in absolute methanol⁹ at 20°. This solution was filtered, cooled to 0°, and an equal volume of ice-water added with good stirring and efficient cooling.

(1) This work was supported by the Office of Naval Research.

(2) Reported in part at the Northwest Regional Meeting of the ACS, June, 1951, Seattle, Washington.

(3) F. H. Malpress and A. B. Morrison, *Biochem. J.*, **46**, 307 (1950).

(4) M. Rogosa, *J. Biol. Chem.*, **175**, 413 (1948).

(5) F. J. Reithel, M. G. Horowitz, H. M. Davidson and G. W. Kittinger, *ibid.*, **194**, 839 (1952).

(6) M. E. Krahl and C. F. Cori, "Biochemical Preparations," Vol. 1, John Wiley and Sons, New York, N. Y., 1949, p. 33.

(7) T. Posternak, *THIS JOURNAL*, **72**, 4824 (1950).

(8) F. J. Reithel, *ibid.*, **67**, 1056 (1945).