solvent is doubtless extremely low; its value cannot be determined readily.

It is a striking fact that, while the conductance of aluminum bromide is greatly increased for ether additions above a molar ratio of unity, with the methyl derivatives, the conductance remains constant for ratios greater than unity. This would seem to indicate that only one of the three bromine atoms of aluminum bromide is labile and replaceable by a molecule of ether. In any case, with these compounds there seems to be no interaction between ether and the monoetherate of the monomer.

V. Summary

1. On addition of dimethyl ether, the conductance of aluminum bromide in methyl bromide decreases to a minimum value for a molar ratio of ether to salt slightly less than unity. On further addition of small quantities of ether, the conductance increases sharply and thereafter increases approximately as a linear function of the added ether.

2. The conductance of methylaluminum dibromide and of dimethylaluminum bromide passes through a maximum and thereafter decreases to a value slightly above that of the pure salts at a molecular ratio of unity. On further addition of ether, the conductance remains unchanged.

3. The presence of a maximum in the conductance curves of the methylated compounds indicates the existence of these substances in solution as dimers and that these dimers form etherates which are better conductors than the pure salts or their monoetherates.

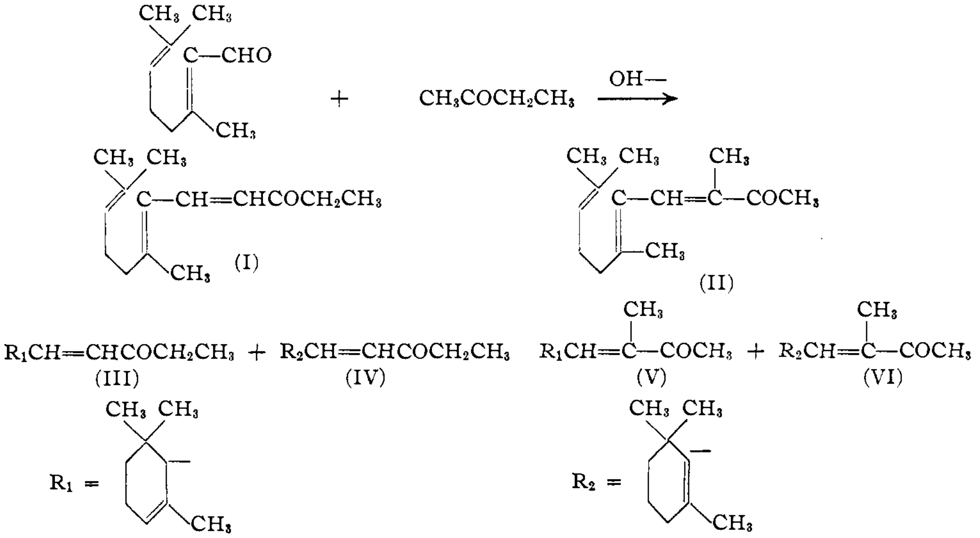
PROVIDENCE, R. I. RECEIVED FEBRUARY 25, 1949

[CONTRIBUTION FROM TRUBEK LABORATORIES]

Ultraviolet Absorption Spectra in the Methyl Ionone Series

BY R. M. LUSSKIN AND LEONARD WINSTON

It has been demonstrated[1] that the condensation of citral and methyl ethyl ketone leads to a mixture of pseudomethylionones, (I) and (II), from which, by acid catalyzed cyclization, four methylionones, (III), (IV), (V) and (VI) are derived. Naves and Bachmann[2] have reported the absorption spectrum of α-*i*-methylionone (V), but the range in which the measurement was taken did not include the wave length of maximum absorption. Ultraviolet absorption spectra of the four methyl ionones and the two pseudo methylionones have now been determined, and the position of the maxima correlated with the structure of the chromophores.



The absorption peaks of the alpha isomers agree with Woodward's[3] generalization for the absorption of alpha-beta unsaturated ketones. α-*n*-Methylionone (III), a monosubstituted ketone, exhibits maximum absorption at 228 mμ, and α-*i*-methylionone, disubstituted, at 235 mμ.

From the values obtained in the present work and from those reported in the literature for similar compounds, it is observed that disubstituted dienones show an $\epsilon_{(\max)}$ at 291 ± 1 mμ and trisubstituted at 294 ± 2 mμ (Table I).

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[1] Koster, *Ber.*, **80**, 248 (1947).

[2] Naves and Bachmann, *Helv. Chim. Acta*, **26**, 2151 (1943).

[3] Woodward, THIS JOURNAL, **64**, 76 (1942).

The differences (2–6 mμ) are small and, therefore, in disagreement with the values obtained by Evans and Gillam[4] and, more recently, by L. Fieser, M. Fieser and Rajagopalan[5] for compounds in the steroid series. The latter workers postulated that introduction of an alkyl group exerts a bathochromatic effect on an enone or dienone of 10, 12 or 18 mμ, depending on the position of substitution.

TABLE I

DISUBSTITUTED COMPOUNDS

	Max. abs. (mμ)
Pseudoionone	292
n-Methylpseudoionone (I)	292
Citrylidineacetaldehyde[6]	290
TRISUBSTITUTED COMPOUNDS	
i-Methylpseudoionone (II)	293.5
β-Ionone[7]	296
β-*n*-Methylionone (IV)	295
β-Cyclocitrylidineacetaldehyde[8]	293
β-Irone[9]	295

TABLE II

PHYSICAL PROPERTIES OF THE METHYL IONONES

Methylionone	Max. abs.	ε	n_{20}	d_{20}	Exaltation
α-*n*- (III)	228.5	13600	1.4980	0.9386	0.7
β *n*- (IV)	295	9390	1.5155	.9370	2.7
α-*i*- (V)	235	15000	1.5008	.9303	1.5
β-*i*- (VI)	228	11600	1.5053	.9376	1.2

The absorption maximum of the so called β-*i*-methylionone (228 mμ), differs so markedly from dienones that it is questioned whether formula (VI) represents the correct structure. Rather, the compound appears to be a disubstituted enone, an ionone of the "alpha" type. The molecular exaltation (Table II), is also an argument against the dienone formulation, for the value obtained, 1.2 (reported value = 1.5[1]), is that of a singly conjugated system. The homogeneity of the preparation was assumed from the sharpness of melting point of the semicarbazone (181°) and from the constant refractive index of the ketone regenerated from it.

Experimental

α-*n*-Methylionone (III).—Five hundred grams of "Methyl Ionone" (prepared from pseudomethylionone[1] by cyclization with phosphoric acid),[10] 1500 g. of 37% sodium bisulfite solution, 115 g. of ammonium chloride and 25 g. of sodium hydroxide were refluxed for sixteen hours. The solution was cooled to 50°, 6875 g. of water added, and the insoluble, crude α-*i*-methylionone separated. After two extractions with 750 cc. of benzene, 937.5 g. of sodium carbonate was added to the aqueous solution of the *n*-methyl isomer which was then refluxed for three and one-half hours. The oil layer was collected and the waters extracted with 625 cc. of benzene. After combining the oil and benzene extracts and washing with four portions of 600 cc. of water, the solvents were removed by distillation at 40 mm. The residual oil was distilled and refractionated with a 16″ jacketed column packed with glass beads to give 63.3 g. of product, b. p. 72–76° at 0.5 mm., n_{20} 1.4980. The semicarbazone melted at 143–144° (reported m. p. 145°[1]).

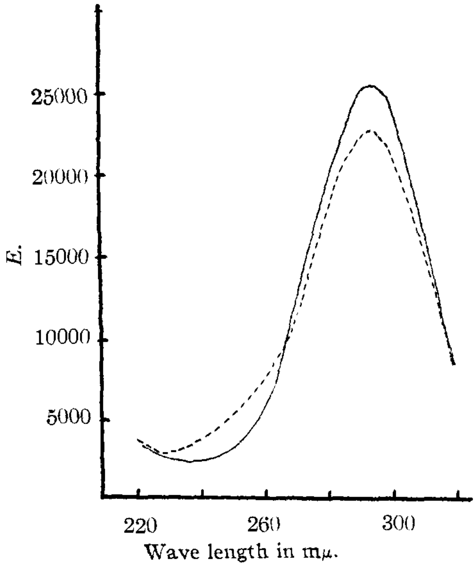

Fig. 1.—Ultraviolet absorption spectra of the pseudomethylionones: *iso*-pseudomethylionone, ———; *n*-pseudomethylionone, - - - - - .

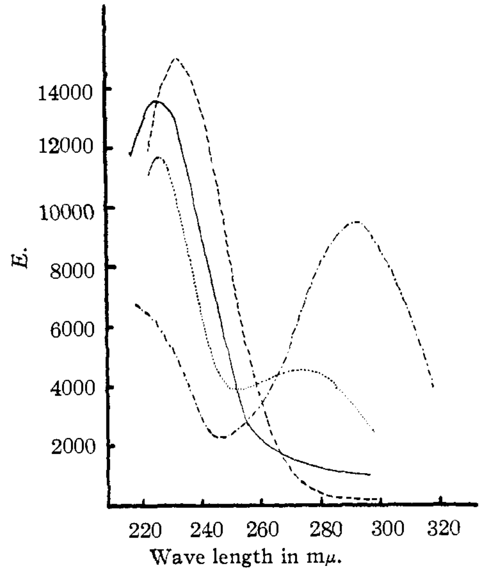

Fig. 2.—Ultraviolet absorption spectra of the methylionones: α-*n*-methylionone, ———; β-*n*-methylionone, - - - - - -; α-*i*-methylionone, - - - -; β-*i*-methylionone, ...

β-*n*-Methylionone (IV).—The above procedure for the bisulfite purification was repeated with 500 g. of "methyl ionone beta," prepared by the cyclization of pseudomethyl-

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(4) Evans and Gillam, *J. Chem. Soc.*, 432 (1945).

(5) L. Fieser, M. Fieser and Rajagopalan, *J. Org. Chem.*, **13**, 800 (1948).

(6) Burawoy, *J. Chem. Soc.*, 20 (1941).

(7) Young, Cristol, Andrews and Lindenbaum, THIS JOURNAL, **66**, 855 (1944).

(8) Barraclough, Batty, Heilbron and Jones, *J. Chem. Soc.*, 1549 (1939).

(9) Naves, *Helv. Chim. Acta*, **31**, 893 (1948).

(10) Hibbert and Cannon, THIS JOURNAL, **46**, 119 (1924).

ionone under the same conditions employed for β-ionone.[11] After separating the insoluble β-*i*-methylionone, the *n*-methyl isomer was regenerated from the bisulfite solution. Final fractionation yielded 160.0 g. of β-*n*-methylionone, b. p. 86–88° at 1 mm., n_{20} 1.5155. The m. p. of the semicarbazone was 145° (reported m. p. 145°[1]).

β-*i*-Methylionone (VI).—Starting with 90 g. of crude β-*i*-methylionone the semicarbazone was prepared and hydrolyzed according to Young's procedure[7] for the purification of β-ionone. The yield of β-*i*-methylionone semicarbazone after two recrystallizations from 60% alcohol was 49 g. (42.5% yield) melting at 181° (cor.) (reported m. p. 183°[1]). Hydrolysis of 40 g. of the semicarbazone gave 18.3 g. of distilled β-*i*-methylionone and 13.2 g. of unchanged semicarbazone (m. p. 179–181°). Based on the semicarbazone that reacted the yield was 87%. The hydrolyzed material was fractionated with a 12″ column packed with glass helices and yielded 11.1 g., b. p. 78° at 0.5 mm., n_{20} 1.5051–1.5054.

α-*i*-Methylionone (V).—The semicarbazone of crude α-*i*-methylionone was prepared by the same procedure. Four recrystallizations from 70% alcohol gave a 46% yield of semicarbazone melting at 203.5° (cor.) (reported m. p. 203°[1]). Thirty-eight grams of the semicarbazone, 80 cc. of benzene, and 165 g. of 30% phosphoric acid were refluxed for twelve hours. Seven and five-tenths grams of starting material (m. p. 202.5°) was collected by filtration. The benzene layer was separated, washed with sodium carbonate solution, and the solvent removed by distillation at 40 mm. Distillation of the residue gave 13.2 g. of α-*i*-methylionone (55% yield based on the semicarbazone that reacted) which was fractionated with a 10″ column packed with glass helices. Eight and two-tenths grams was obtained, b. p. 83° at 1 mm., n_{20} 1.5008.

Pseudoionone (b. p. 107° at 1 mm., n_{20} 1.5339), ***n*-methylpseudoionone** (I) (b. p. 115–116° at 1 mm. n_{20} 1.5281) and ***i*-methylpseudoionone** (II) (b. p. 118 at 1 mm., n_{20} 1.5265) were purified through the bisulfite compound using the same procedure as given for α-*n*-methylionone.

The pseudomethylionones and the methylionones are commercially available compounds. Absorption spectra were determined in 95% ethanol by means of a Beckman spectrophotometer.

Summary

The ultraviolet absorption spectra have been determined for *i*-methylpseudoionone, *n*-methylpseudoionone and the four methylionones derived from them.

The position of the band maxima has been correlated with the structure of the chromophore.

Spectrophotographic evidence suggests that the structure previously assigned to "beta-*i*-methylionone" is incorrect.

EAST RUTHERFORD, N. J. RECEIVED DECEMBER 20, 1948

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(11) Royals, *Ind. Eng. Chem.*, **38**, 546 (1946).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, PARKE, DAVIS & CO.]

The Ultraviolet Absorption Spectra of Simple Unsaturated Compounds. II. *m*- and *o*-Disubstituted Benzene Derivatives

BY LEONARD DOUB AND J. M. VANDENBELT

In the previous paper of this series[1] on simple benzene compounds it was shown that the longer wave length maxima of the mono- and *p*-disubstituted derivatives could be related to the parent bands of benzene near 200 mμ and at 254 mμ, called the first primary and the secondary bands, respectively. In addition, with derivatives showing considerably displaced absorption, a third band appeared at short wave length which was termed the second primary band. The present study indicates that the concepts developed there can be applied to an analysis of the spectra of *m*- and *o*-disubstituted benzene derivatives.

Methods and Materials.—A Model DU Beckman quartz spectrophotometer with hydrogen discharge tube source was used for all measurements. Extinction coefficients were calculated by dividing the density observed in matched cells by the molar cell concentration. Band peaks were read in the density range 0.4–0.8 at a spectral band width of approximately 1 mμ. Readings at extremely low wave lengths were obtained by balancing the instrument for 100% transmission through the solvent cell at the 0.1 switch position. To indicate a decreased accuracy at the end of the accessible region, principally as a result of the increase in scattered radiation, some values in Table I are given in italics.

Melting points of solids after recrystallization and the boiling points of liquids upon distillation were accepted as confirmation of identity and purity. Water was used as the solvent throughout. With substances relatively insoluble in water, methanol was used first for solution, followed by a larger dilution in water. A blank containing an equal amount of methanol was prepared for instrument reading. The methanol concentration was restricted to 1 or 2% in these cases.[2]

Presentation of Data.—Figure 1 gives curves of *m*- and *o*-hydroxyacetophenone which serve to illustrate the absorption characteristics of this general class of compounds. It can be seen that there is considerable similarity in the spectra of these derivatives. The pattern exhibited is that of three bands decreasing in intensity with displacement in an almost stepwise fashion from a rather intense short wave length band. The displacement of the bands upon ionization is similar to that observed in mono- and *p*-disubstituted

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(1) Doub and Vandenbelt, THIS JOURNAL, **69**, 2714 (1947).

(2) The spectra of many of the compounds given here have been reported previously in the literature. However, the diversity of solvents and uncertainty below 220 mμ justify repetition for this study.