

TABLE VII

RUN 111. EXCHANGE OF 0.119 *M* TRIETHYLAMMONIUM CHLORIDE WITH METHANOL IN METHANOL SOLUTION CONTAINING 0.0105 *M* HYDROGEN CHLORIDE AT 0°

Time, <sup>a</sup> sec.	<i>d</i> , <sup>b</sup> sec.	D, <sup>c</sup> %	Hg- (NO <sub>3</sub> ) <sub>2</sub> , <sup>d</sup> ml.	D/Hg- (NO <sub>3</sub> ) <sub>2</sub> , <sup>e</sup> %/ml.	Reac- tion, <sup>f</sup> %	<i>k</i> <sub>o</sub> , <sup>g</sup> sec. <sup>-1</sup> × 10 <sup>3</sup>
0	...	...	..	0.1540	0.0	..
55	73.7	0.260	3.28	.0793	48.5	..
91	68.7	.306	4.71	.0650	57.8	5.5
125	75.0	.249	4.72	.0528	65.7	6.1
166	83.3	.188	4.56	.0413	73.1	6.0
211	91.5	.140	4.47	.0313	79.6	6.2
269	99.0	.104	4.61	.0226	85.3	5.6
2000	131.0	.000	..	.000	100.0	..

<sup>a</sup> Between mixing reactants and adding aliquot to precipitating medium. <sup>b</sup> Average dropping time of the water obtained by equilibrating the precipitated salt with 0.46 ml. of conductivity water, separating the water and purifying it. <sup>c</sup> Atom per cent. deuterium in the water obtained from difference of reciprocals of dropping times (*d*) of water sample and conductivity water (*d* = 130.6) and the calibration curve. <sup>d</sup> Ml. of 0.106 *N* (0.053 *M*) Hg(NO<sub>3</sub>)<sub>2</sub> used to titrate salt equilibrated with water. <sup>e</sup> Ratio of two previous columns. <sup>f</sup> Percentage of the total variation (0.1540) in the previous column that has occurred. The initial % D/ml. Hg(NO<sub>3</sub>)<sub>2</sub> was calculated from an analysis on the dried salt used, which contained 74.2 atom % exchangeable deuterium. The final % D/ml. corresponds to 100.5%

reaction assuming random distribution of deuterium among the exchangeable hydrogens, but the experimental error is more than 1%. <sup>g</sup> Experimental first-order rate constant identical with *k*<sub>o</sub> of equation 1 in reference 2. Calculated, in this table only, from the formula  $k_o = 2.303 \log [(1 - F_1)/(1 - F_2)]/(t_2 - t_1)$ , where *F* = % reaction/100, from successive pairs of kinetic points to magnify trends. Ordinarily *k*<sub>o</sub> was evaluated instead by the graphical method described under "analysis of kinetic data."

In a number of cases the straight line did not pass through zero % reaction at zero time. This may be due to several factors. In runs in which the salt was as concentrated as 1 *M*, there was a significant cooling effect; dissolving and warming back to thermostat temperature required about one minute. Furthermore, the reaction is accelerated by dilution with an inert non-polar liquid; this increases rate of exchange during the quenching process unless precipitation is extremely rapid and quantitative. In some of the kinetic runs it was shown by taking aliquots immediately after mixing that as much as 10% exchange occurred in the quenching process, even though 98% of the salt was precipitated. However, the percentage exchange during quenching proved independent of a fivefold variation of initial percentage deuterium in the salt used. These errors in percentage reaction caused by neglecting exchange during quenching affect only the intercept, since the time and conditions of quenching were the same for all aliquots of a given kinetic run. Hence *k*<sub>o</sub> should still be accurate since it is determined from *t*<sub>1/2</sub>, which is a measure of the slope.

A typical kinetic run is presented in Table VII.

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

## The Effects of Substituents at the 1- and 3-Positions on the Visible Absorption Spectrum of Azulene<sup>1</sup>

BY EDWARD J. COWLES

RECEIVED SEPTEMBER 17, 1956

A study is presented of the visible absorption spectra of twelve 1-substituted and 1,3-disubstituted azulenes prepared by electrophilic substitution reactions. For the position of the principal absorption peak, the equation  $(\nu_{\max})^2 = \nu_0^2 (1 + A_1 + A_2)$  fits the data better than the equation  $\lambda_{\max} = \lambda_0 + B_1 + B_2$ , where the *A*'s and *B*'s are constant increments characteristic of substituents, both bathochromic and hypsochromic, at positions 1 and 3. The effects of solvent are discussed briefly.

The visible absorption spectra of the alkyl-substituted azulenes have been studied extensively. Various workers have considered the effects of substituents on the position of the principal absorption peak,<sup>2</sup> on that of the longest-wave length band,<sup>3</sup> and on the "average position" of all the bands of the spectrum.<sup>4</sup> Effects of alkyl substituents at various positions in the azulene nucleus have been found to be additive. The visible spectra have therefore been useful in the identification of natural and synthetic azulenes.

The present paper will be concerned with the position of the principal absorption peak in the visible spectra of 1-substituted and 1,3-disubstituted azulenes prepared by electrophilic substitution reactions.<sup>5-8</sup> Sufficient spectral data to war-

rant a detailed study were available for only the 12 compounds, besides azulene, listed in Table II.

The data were obtained for the compounds in various solvents: petroleum ether, *n*-hexane, cyclohexane, *n*-heptane and chloroform. For the purposes of this study, as is indicated in Table II, the saturated hydrocarbons have been lumped together as a single type of solvent, to be compared or contrasted with the more polar chloroform. The effects of solvent are discussed briefly below.

Not only alkyl groups (including benzyl<sup>7</sup>), but also other *o,p*-directing groups (halogens and acetylaminos<sup>8</sup>) are found to exert a bathochromic effect when substituted at the 1- and 3-positions in the azulene nucleus. On the other hand, *m*-directing groups (acetyl, nitro and carbomethoxy<sup>5,6</sup>), as 1- and 3-substituents, cause a hypsochromic shift of the absorption bands.

In many of these compounds, 1,3-substituents

(1) This work was supported in part by a grant from the Research Corporation.

(2) P. A. Plattner, A. Fürst and K. Jirasek, *Helv. Chim. Acta*, **30**, 1320 (1947).

(3) A. J. Haagen-Smit, *Fortschr. Chem. Org. Naturstoffe*, **V**, 40 (1948).

(4) H. Pommer, *Angew. Chem.*, **62**, 281 (1950).

(5) A. G. Anderson, Jr., and J. J. Tazuma, *THIS JOURNAL*, **75**, 4979 (1953).

(6) A. G. Anderson, Jr., J. A. Nelson and J. J. Tazuma, *ibid.*, **75**, 4980 (1953).

(7) A. G. Anderson, Jr., E. J. Cowles, J. J. Tazuma and J. A. Nelson, *ibid.*, **77**, 6321 (1955).

(8) According to a private communication from A. G. Anderson, Jr., a satisfactory analysis of dinitroazulene has been obtained, and the 1,3-structure of the dinitro and diacetyl derivatives has been proved with reasonable certainty since the publication of the references just cited.

TABLE I  
 INCREMENTS DUE TO VARIOUS 1,3-SUBSTITUENTS

Substituent	Satd. hydrocarbon solvent				Chloroform solvent			
	Eq. 1 <sup>a</sup> <i>B</i> , mμ	Eq. 4 <sup>b</sup> <i>B̄</i> , mμ	Eq. 4 <sup>b</sup> <i>A</i>	Eq. 4 <sup>b</sup> <i>Ā</i>	Eq. 1 <sup>a</sup> <i>B</i> , mμ	Eq. 4 <sup>b</sup> <i>B̄</i> , mμ	Eq. 4 <sup>b</sup> <i>A</i>	Eq. 4 <sup>b</sup> <i>Ā</i>
Benzyl	+25	..	-0.081	.....	+20	+19	-0.066	-0.066
Bromo	+25	+23	- .081	-0.072	+19	+19	- .063	- .069
Chloro	+30	+30	- .096	- .089	..	..	.....	.....
Acetyl	-30	..	+ .112	.....	-41	-37	+ .159	+ .152
Nitro	-48	..	+ .189	.....	-62	-54	+ .255	+ .234

<sup>a</sup>  $\lambda_{\max} = \lambda_0 + B_1 + B_3$ . <sup>b</sup>  $\lambda_{\max} = \lambda_0/\sqrt{1 + A_1 + A_3}$ .

 TABLE II  
 POSITION OF PRINCIPAL ABSORPTION PEAK IN SPECTRA OF SUBSTITUTED AZULENES

Substituents at 1-position or at 1,3-positions	Satd. hydrocarbon solvent					Chloroform solvent				
	$\lambda_{\max}$ exptl., mμ	Eq. 1 <sup>a</sup> From <i>B</i> 's	Eq. 4 <sup>b</sup> From <i>B̄</i> 's	Eq. 4 <sup>b</sup> From <i>A</i> 's	Eq. 4 <sup>b</sup> From <i>Ā</i> 's	$\lambda_{\max}$ exptl., mμ	Eq. 1 <sup>a</sup> From <i>B</i> 's	Eq. 4 <sup>b</sup> From <i>B̄</i> 's	Eq. 4 <sup>b</sup> From <i>A</i> 's	Eq. 4 <sup>b</sup> From <i>Ā</i> 's
None	580	..	..	..	..	577	..	..	..	..
Benzyl	605	..	..	..	..	597	..	596	..	597
Bromo	605	..	603	..	602	596	..	596	..	598
Chloro	610	..	610	..	608	..	..	..	..	..
Acetyl	550	..	..	..	..	536	..	540	..	538
Nitro	532	..	..	..	..	515	..	523	..	519
Dibromo	625	630	626	634	627	619	615	615	617	621
Dichloro	638	640	640	645	640	..	..	..	..	..
Diacetyl	..	..	..	..	..	505	495	503	503	505
Dinitro	..	..	..	..	..	478	453	469	470	476
Acetyl, benzyl	..	..	..	..	..	557	556	559	552	554
Bromo, chloro	635	635	633	639	633	..	..	..	..	..
Bromo, nitro	..	..	..	..	..	538	536	542	528	535

<sup>a,b</sup> See footnotes to Table I.

show simple additive effects on the  $\lambda_{\max}$  of the principal absorption peak, as expressed by

$$\lambda_{\max} = \lambda_0 + B_1 + B_3 \quad (1)$$

where  $\lambda_0$  is the  $\lambda_{\max}$  for azulene in the particular solvent used, and  $B_1$  and  $B_3$  are constant increments characteristic of the substituents at positions 1 and 3, respectively. In other compounds, however, notably the dinitro and diacetyl derivatives, the deviations are large. Two reasons for the discrepancies may be suggested:

First, equation 1 omits the interaction of a 3-substituent with the 1-substituent as well as the azulene nucleus. Stated more generally, because of the restricted quantity of data, equation 1 necessarily omits the higher-order terms in the general equation which might be used

$$\lambda = \lambda_0 \left[ 1 + \frac{\partial \lambda}{\partial b} \delta b_1 + \frac{\partial \lambda}{\partial b} \delta b_3 + \frac{\partial^2 \lambda}{\partial b^2} (\delta b_1)^2 + \frac{\partial^2 \lambda}{\partial b^2} (\delta b_3)^2 + \frac{\partial^2 \lambda}{\partial b_1 \partial b_3} (\delta b_1)(\delta b_3) + \dots \right] \quad (2)$$

where  $b$  is the "bathochromicity" of a substituent (and may be either positive or negative), and subscripts 1 and 3 refer to positions 1 and 3. These higher-order terms will be especially significant when the increment of  $\lambda_{\max}$  is large, as in dinitroazulene.

Second, the actual electron transitions corresponding to various absorption bands are not known. The strongest peak in one spectrum may therefore not represent the same transition as the strongest peak in another, although there can be little doubt in those cases in which the structure of the entire band envelope is retained. This is not always

true, however, particularly of the compounds with hypsochromic substituents, which tend to obliterate the fine structure of the absorption spectrum.<sup>9</sup>

The foregoing discussion leaves unanswered, however, the question whether the wave length or the frequency of the absorption band should be considered. As Table II shows, one obtains, overall, considerably better correlation of the spectra considered here by using the square of the frequency than by using the first power of the wave length. That is, one finds reasonably good additive behavior of substituents, including acetyl and nitro, when he uses an equation of the form

$$(\bar{\nu}_{\max})^2 = (1/\lambda_{\max})^2 = \bar{\nu}_0^2 (1 + A_1 + A_3) \quad (3)$$

or alternatively

$$\lambda_{\max} = \lambda_0/\sqrt{1 + A_1 + A_3} \quad (4)$$

where  $A_1$  and  $A_3$  are constant increments characteristic of the substituents at positions 1 and 3, respectively.

**Remarks on Tables I and II.**—In Table I are listed, for five substituents, the characteristic  $B$ 's calculated on the basis of equation 1 and the  $A$ 's calculated on the basis of equation 3, from the experimental data in Table II.

In all calculations the experimental  $\lambda_0$ 's for unsubstituted azulene in hydrocarbon solvents and in chloroform are accepted as correct. The  $B$ 's and  $A$ 's are increments calculated from the  $\lambda_{\max}$ 's of the monosubstituted derivatives only as com-

(9) The visible spectrum of such a compound (e.g., 1-nitroazulene) may consist simply of a broad hump; one is forced to consider the top of this hump as the " $\lambda_{\max}$  of the principal absorption peak."

pared with  $\lambda_0$  for the solvent in question. For example, for the nitro group in chloroform solvent

$$B = 515 - 577 = -62 \text{ m}\mu; A = 577^2/515^2 - 1 = 0.255$$

The  $\bar{B}$ 's and  $\bar{A}$ 's are average values calculated by least squares from all pertinent experimental data in Table II. Thus, for the nitro group in chloroform solvent,  $\bar{B}$  and  $\bar{A}$  are calculated from the experimental  $\lambda_{\text{max}}$ 's for azulene and for the mononitro, dinitro, monobromo, dibromo and bromonitro derivatives.

The calculated  $\lambda_{\text{max}}$ 's based on these empirical  $B$ 's,  $A$ 's,  $\bar{B}$ 's and  $\bar{A}$ 's are obviously empirical also. Naturally, over-all, the  $\lambda_{\text{max}}$ 's calculated from the  $\bar{B}$ 's and  $\bar{A}$ 's agree better with the experimental  $\lambda_{\text{max}}$ 's than do the  $\lambda_{\text{max}}$ 's calculated from the  $B$ 's and  $A$ 's.

Equation 3 or 4 might be obtained by considering the  $\pi$ -electron system of azulene, or the center of gravity of the  $\pi$ -electrons,<sup>10</sup> as a simple harmonic oscillator, for which the frequency of absorbed light would be given by an equation of the type<sup>11</sup>

$$\bar{\nu} = \sqrt{\frac{k}{m}} / 2\pi c \quad (5)$$

(10) Cf. W. T. Simpson, *J. Chem. Phys.*, **16**, 1124 (1948).

(11) Cf. G. N. Lewis, *Chem. Revs.*, **25**, 273 (1939); also K. Hirayama, *THIS JOURNAL*, **77**, 373 (1955).

If, in the azulene system, the mass  $m$  of the oscillator may be considered constant, and if 1- and 3-substituents increase or decrease  $k$  in a simple additive fashion, then equation 5 leads directly to equation 3 or 4.

For the discrepancies between the experimental values of  $\lambda_{\text{max}}$  and the values calculated on the basis of equation 3 or 4, the same reasons may be advanced, of course, as for the discrepancies resulting from the use of equation 1.

**Effects of Solvent.**—Table I shows that, as compared with the saturated hydrocarbons, the more polar solvent, chloroform, markedly increases the hypsochromic effect of *m*-directing groups but decreases the bathochromic effect of *o,p*-directing groups.

As expected, chloroform (as well as alcohol) also tends to destroy the fine structure exhibited by the spectra of many of these compounds in alkane solutions. Chloroform is preferable, however, in the respect that some of the substituted azulenes, such as the dinitro compound, are readily soluble in chloroform but practically insoluble in saturated hydrocarbons.

**Acknowledgment.**—The author expresses his appreciation for many suggestions received from Dr. A. G. Anderson, Jr., and Dr. W. T. Simpson. DULUTH 5, MINN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

## Sterol Models. I. 3a-Methyl-*cis*- and -*trans*-hexahydroindans and their -3a-Methyl-*d*<sub>3</sub> Analogs<sup>1</sup>

BY RICHARD L. KRONENTHAL<sup>2</sup> AND ERNEST I. BECKER<sup>3</sup>

RECEIVED JULY 5, 1956

The independent and unequivocal syntheses of 3a-methyl-*cis*- and -*trans*-hexahydroindan and several of their deuteromethyl analogs have been achieved through stereospecific reactions. Through a Diels-Alder synthesis, a methoxycarbonyl group was locked into the *cis*-configuration at the angular position of a tetrahydroindan and transformed, *via* the saturated angular ester, hydroxymethyl and corresponding tosylate of the latter, to the desired 3a-methyl-*cis*-hexahydroindan. By employing the appropriate combinations of lithium aluminum hydride and lithium aluminum deuteride, the mono-, di- and trideuteromethyl-*cis*-hexahydroindans also were obtained. 3a-Methyl-*trans*-hexahydroindan was attained through 4a-ethoxycarbonyl-*trans*-3,4,4a,5,6,7,8,8a-octahydro-2-[1H]-naphthalenone. After the oxo group was converted to the corresponding dioxolane, the angular ester was reduced to the hydroxymethyl group and then to the angular methyl group through the tosylate and benzyl thioether. After hydrolysis of the dioxolane, the resulting methyldecalone was oxidatively cleaved, recycled to the corresponding hydrindanones and finally reduced to 3a-methyl-*trans*-hexahydroindan. By starting with the dioxolane ester and using lithium aluminum deuteride and deuterated Raney nickel, the corresponding deuterium containing analogs were obtained.

### Introduction

Until it was shown in the present work that butadiene could be made to undergo an unequivocal *cis*-addition to a cyclopentenodienophile resulting in an angularly substituted *cis*-tetrahydroindan, no direct stereospecific synthesis of a *cis*- or a *trans*-hexahydroindan containing a substituent only at 3a- had been reported.<sup>4</sup> In almost all other

routes described in the literature,<sup>5-8</sup> both isomers may be formed with one usually predominating. Because the ultimate aim of the present work was to obtain compounds for infrared studies and because infrared determinations are, in general, sensitive enough to be affected by small amounts of impurities, the previously available route to the

(1) (a) This work was supported by the National Institutes of Health, Grant G-3124. (b) Presented in part at the 127th Meeting of the American Chemical Society, March 29–April 7, 1955, Cincinnati, Ohio, Abstracts, 49-N.

(2) Taken from the Dissertation submitted to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1955.

(3) To whom inquiries should be directed.

(4) Stereospecific syntheses of more highly substituted hexahydroindans

have been accomplished; cf. E. Dane, J. Schmitt and C. Rautenstrauch, *Ann.*, **532**, 29 (1937), and W. Bockemuller, U. S. Patent 2,179,809; *C. A.*, **34**, 1823 (1940).

(5) For earlier references, see E. Josephy and F. Radt, "Elsevier's Encyclopaedia of Organic Chemistry," Vol. XIIA, p. 105 ff.

(6) W. E. Bachmann and E. K. Raunio, *THIS JOURNAL*, **72**, 2530 (1950).

(7) C. A. Grob and J. A. Rumpf, *Helv. Chim. Acta*, **37**, 1479 (1954).

(8) D. K. Banerjee and P. R. Schefer, *THIS JOURNAL*, **72**, 1931 (1950).