Anal. Subs., 0.1000: 5.60 cc. of 0.0714 *N* NaOH. Calcd. for $C_{29}H_{30}O_4N_2$: N, 5.95. Found: 5.60.

Heptane-diol Diacetate.—The substance boils at 113–113.5° at 1 mm.; 249–252° at 748 mm.; n^{25}_D, 1.4268; d^{20}_{20}, 0.9934; d^0_0 1.0135.

Anal. Subs., 0.1019: CO_2, 0.2280; H_2O, 0.0876. Calcd. for $C_{11}H_{20}O_4$: C, 61.08; H, 9.28. Found: 61.05, 9.62.

Summary

1. The reduction of furfuracrolein in alcohol solution was carried out using platinum-oxide platinum black as a catalyst and a little ferrous sulfate as a promoter. After the absorption of 3 molecular equivalents of hydrogen, there was isolated furylpropyl alcohol and tetrahydrofurylallyl alcohol. After absorption of 4.2–4.4 molecular equivalents of hydrogen, the maximum amount taken up, there was obtained tetrahydrofurylpropyl alcohol and a heptane-diol.

2. An attempt to isolate products after the absorption of one molecular equivalent or two molecular equivalents of hydrogen was unsuccessful. If the reduction was carried out in the presence of ferrous sulfate and zinc acetate, however, the reduction stopped automatically after one molecular equivalent of hydrogen had been absorbed and pure furylallyl alcohol was readily obtained.

3. The acetates of many of the alcohols were prepared and the α-naphthyl urethans of some of them.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE SPECTROGRAPHIC LABORATORY OF THE DEPARTMENT OF PHYSICS, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

ULTRAVIOLET ABSORPTION SPECTRA OF CYCLOHEXENE, ETHYL ETHER, METHYL-NORMAL-AMYL ETHER AND ETHYLENE CHLOROHYDRIN. A CORRECTION TO THE ARTICLE OF THIS TITLE BY SMITH, BOORD, ADAMS AND PEASE

BY HENRY DE LASZLO[1]

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The ultraviolet absorption spectra of a large number of colorless aliphatic and aromatic compounds have been studied by Henri and his coworkers. One of the main results of this very careful examination was that while benzene possesses some very well marked bands in the region λ2600 Å.–λ2400 Å., the saturated cyclic and open-chain aliphatic hydrocarbons are transparent in this portion of the spectrum. Even decahydronaphthalene[2] absorbs only from 2300 Å. downwards. The intro-

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[1] Research Associate, Department of Physics, Massachusetts Institute of Technology.

[2] De Laszlo, *Proc. Roy. Soc.* (London), **111A**, 376 (1926).

duction of one double bond in an otherwise saturated molecule gives rise to only broad absorption bands both in vapor and in solution.

All saturated aliphatic alcohols so far examined show no absorption above λ2400 Å.; below this they all have a very broad absorption band, the position of whose maximum varies from λ2200 Å. to λ2350 Å., passing from methyl to butyl alcohol. The introduction of a halogen does not, as a rule, alter the general appearance of the spectrum, but if any bands were present in the original substance, these will be displaced toward the visible[3] by an amount depending on the size of the molecule. Pure ethyl ether shows no absorption above 2100 Å., even the liquid being perfectly transparent in a thickness of 40 mm. In fact, ethyl ether and hexane have been used as solvents for the past years in the measurement of ultraviolet absorption spectra.[4] The higher aliphatic ethers will show a slight shift toward the red, the absorption limit depending on the number of CH_2 groups in the molecule.

Benzene vapor possesses a very characteristic absorption spectrum consisting of more than 400 lines and band-heads. Of the 200 substances possessing a measurable absorption that have been examined by Henri and his pupils, no two were found to have identical spectra. Nor is this in any degree probable when one considers the very complicated mechanism that gives rise to these spectra.

If, therefore, the work of Smith, Boord, Adams and Pease, published in THIS JOURNAL, 1927, page 1335, were correct, then all previous experimental data would be false, which is hardly possible. These four authors find absorption spectra identical to that of benzene for the following substances: cyclohexene, ethyl ether, ethylene chlorohydrin and methyl-*n*-amyl ether. These, however, all fall into the categories mentioned above and will, therefore, show no absorption between λ2600 Å. and λ2400 Å.

In order to confirm this, we have examined ethylene chlorohydrin in vapor and in liquid phase.

Experimental Work

One hundred grams of Eastman Kodak Company ethylene chlorohydrin was rapidly distilled in an all-glass Witmer fractionating apparatus. The portion boiling from 128.7 to 128.8° at 764 mm. was collected. This fraction was colorless and possessed only a very faint alcoholic odor. The absorption spectrum of the vapor was then photographed in a layer 15 cm. thick at temperatures varying from 50 to 110° by steps of 10°. No appreciable absorption above 2250 Å. was to be seen.

The pure liquid was examined in thicknesses of $^1/_{10}$ to 5 mm. Con-

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[3] De Laszlo, *Proc. Roy. Soc.*, (London), **111A**, 359 (1926).

[4] Castille and Henri, *Bull. soc. chim. biol.*, **6**, 299–304 (1924).

tinuous absorption below 2300 Å. was observed for a layer 4 mm. thick. A detailed description of the technique will be given in a later article. Hence, it is clear that pure ethylene chlorohydrin does not absorb appreciably above 2300 Å., and then only in a perfectly continuous manner.

Results

It is obvious, therefore, that in every case mentioned by these authors benzene vapor was present. To show how strong the bands of benzene are, we may state that at a pressure of 0.01 mm. the following five band-heads are still visible as five lines: λ2589.03 Å., λ2528.57 Å., λ2471.03 Å., λ2415.91 Å., λ2363.55 Å. In other words, it has been found that a mass of benzene as small as $^1/_{10,000}$ mg. will still give rise to its characteristic band-heads.

All this goes to show how rigorous must be the purification of those compounds whose absorption spectra are to be determined. Thus, in the case of the substances in question, the distillation should be conducted in an all-glass apparatus with an efficient distilling column of the type developed by Witmer.[5] The boiling-point range should be $\pm ^1/_{10}°$ and this fraction should consist of a major portion of the sample. Wherever possible it has been found best to follow this with three or four crystallizations out of optically pure hexane[4] at about —100°. Chemical purification is also advantageous when possible, as shown in the case of cyclohexane where the benzene present was removed by washing with sulfuric acid. The apparatus for vaporizing and photographing the substance must, of course, be scrupulously clean and is best made entirely of fused quartz so that drastic cleansing with sulfuric and chromic acids may be resorted to.

Aside from the fact that these authors erroneously ascribe the ultraviolet benzene bands to other compounds than benzene, their attempted correlation of the vibrational constants with those of the infra-red bands observed by Ellis[6] seems open to serious objections; for although the theory of polyatomic band spectra is not yet sufficiently developed to account for the empirical form of Henri's equation for band-heads, involving two sets of integral "quantum numbers," it is probable that the observed vibrational constants are characteristic of the *excited* electronic state. At room temperature we should expect only transitions from the zero vibrational level of the initial (normal) state to be of appreciable intensity in absorption. On the other hand, the infra-red vibration-rotation bands involve only the vibrational terms of the *normal* state, and thus should not in general give constants related to those of the ultraviolet absorption bands. The only satisfactory correlation of electronic

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[5] Dis. Zürich Eidg. Tech. Hochschule, **1924**.

[6] Ellis, *Phys. Rev.*, **27**, 298 (1926).

bands with those of the infra-red seems at present to be that given by Birge,[7] in which the constants of the normal state of carbon monoxide, determined from the emission spectrum, are successfully used to compute the positions of the three strongest vibration-rotation bands.

The agreements which are shown in Table II, p. 1344, of the article under discussion are certainly not convincing. The band of longest wave length in the series found by Ellis is that at 6.7μ, which he interprets as the "fundamental" (0 $\longrightarrow$ 1) band. The remaining "observed values" in the table should not exist on this interpretation (unless they are combination bands) and, since they are not included by Ellis, must be of small intensity. However, it is precisely the bands of shorter wave length than 6.7μ which require unreasonably large values of n_1 and n_2 for representation by Henri's formula. In fact, with an equation of two independent variables, any other values for the coefficients may be used and still, with suitable assignments of n_1 and n_2, be made to yield wave lengths which agree as well as those shown. As an illustration we may assume the relation $\nu n = 1000 n_1 + 100 n_2$ and find the following agreements.

TABLE I

n_1	n_2	(obs.)	("calcd.")	("calcd." Smith, etc.)
15	18	0.760	0.758	0.760
13	10	.835	.834	.831
12	10	.913	.910	.910
11	12	1.022	1.021	1.022
9	5	1.172	1.177	1.166
8	7	1.379	1.370	1.370
7	11	1.695	1.695	1.684
5	4	2.16	2.17	2.19
5	10	2.49	2.50	2.45
4	4	2.75	2.78	2.74
4	9	3.25	3.23	3.28
2	2	5.40	5.56	5.53
2	5	6.7	6.7	6.6

We do not agree, therefore, that the authors have "thus disposed of the physical significance of the ultraviolet absorption of these compounds." There can be no doubt, however, that the use of two sets of integers covering a limited range of small values is significant as permitting a satisfactory representation of a large number of the ultraviolet benzene bands, and also that the single parabolic series of infra-red bands bears a striking resemblance to the analogous bands of diatomic molecules.

Again, if the experimental data and theoretical conclusions given by these authors are correct, namely, that the C-H linkage gives rise to this identical band structure in four different cases, why then are they not obtained for cyclohexane which contains plenty of these linkages?

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[7] Birge, *Phys. Rev.* **28**, 1157 (1926).

Summary

1. It has been proved that the experimental results of Smith, Boord, Adams and Pease are erroneous on the following grounds.

(a) Past experience has shown that bodies of the type examined show only continuous absorption from 2350 Å. to 2000 Å.

(b) The absorption of two out of the four substances concerned has been measured and no evidence of a benzene-like structure such as is claimed has been found.

(c) It has been pointed out that benzene may have been present as an impurity either in the material or apparatus in amounts sufficient to explain the results reported by these authors.

2. Their theoretical deductions have also been shown to be unconvincing.

3. It has been pointed out that in this type of work absolute purity of the compounds examined and cleanliness of the apparatus used are essential.

Cambridge, Massachusetts

[Contribution from the Pearson Memorial Laboratory of Tufts College]

THE SYNTHESIS OF ALPHA,BETA-DIACYLSTYRENES AND THEIR REACTION WITH HYDROGEN BROMIDE

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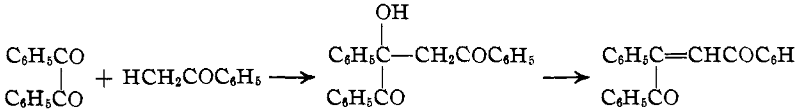
Japp and his co-workers[1] found that in the presence of alcoholic potassium hydroxide, benzil reacts with acetophenone and forms first an addition product (I), and finally an unsaturated diketone (II), which they called anhydracetophenone benzil or α,β-dibenzoylstyrene.[2]



$$\begin{array}{c} C_6H_5CO \\ | \\ C_6H_5CO \end{array} + HCH_2COC_6H_5 \longrightarrow \begin{array}{c} OH \\ | \\ C_6H_5C{-}CH_2COC_6H_5 \\ | \\ C_6H_5CO \\ \text{I} \end{array} \longrightarrow \begin{array}{c} C_6H_5C{=}CHCOC_6H_5 \\ | \\ C_6H_5CO \\ \text{II} \end{array}$$

I II

We have found that many other dibenzoylstyrenes can be made in this manner, but that the reaction is not general. It was possible to substitute for the acetophenone used by Japp a number of other methyl ketones which had alkyl groups or chlorine atoms in the nucleus, while with other closely related methyl ketones the reaction failed. Thus, di-

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[1] Japp and co-workers, *J. Chem. Soc.*, (a) **47**, 35 (1885); (b) **51**, 430 (1887); (c) **53**, 184 (1888); (d) **57**, 662 (1890); (e) **71**, 1138 (1897); *Ber.*, (f) **18**, 187 (1885); (g) **21**, 2933 (1888).

[2] It might better be called phenyldibenzoylethylene, but the naming of compounds substituted in one benzoyl group seems clearer if they are considered as derivatives of styrene.