

for rotatory dispersion. In our case the higher λ_0 value has a definite physical significance corresponding to a known absorption band (2050 Å. for COOH, 2560 Å. for I in 2-methyl-*n*-nonyl iodide). The contribution of the functional group (first term of above formula) is of opposite sign to the contribution of the rest of the molecule (second term). The direction of the first term is to the right and that of the second is to the left. It follows from this that in the levorotatory substances the sign of the contribution of the first band is opposite to the sign of the rotation of the substance observed in the visible. Thus, the sign of the rotation in the visible of the two halides is opposite to the sign of the contributions of Br and of I, which is contrary to the view expressed by W. Kuhn [*Ber.*, **63**, 191 (1930)], whereas in the secondary halides as well as in 1-bromo-3-methylpentane and in 1-iodo-4-methylhexane the direction of the contribution furnished by the halides determines the direction of the rotation in the visible.

The most striking example of the first band exerting a minor influence on the rotation in the visible is given by β -methyl-*n*-valeric acid. With decreasing wave lengths, the rotation increases slowly, reaches a maximum at 2850 Å., decreases sharply to a zero value at 2450 Å. and increases in the opposite direction for still smaller wave lengths. The molecular rotation in heptane is accurately represented ($\pm 1\%$) by the equation

$$[M]^{25} = + \frac{8.088}{\lambda^2 - 0.042} - \frac{11.68}{\lambda^2 - 0.034}$$

The details of this study as well as the results dealing with the influence of the distance of the functional group on the sign of its contribution will be discussed in full in the near future.

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AN ABSOLUTE METHOD FOR ESTABLISHING ORIENTATION IN THE FURAN SERIES

Sir:

Identification of the simpler substitution products of furan, such as the methylated and halogenated furans, is not readily accomplished on account of the difficulty of obtaining solid derivatives from them. The observation that addition of maleic anhydride to furan and certain substituted furans¹ gives rise to crystalline solids, has led us to investigate this reaction as a general method for the identification of furan derivatives.² We have found that addition of maleic anhydride occurs with a variety of substituted

(1) Diels and Alder, *Ber.*, **62**, 554 (1929); Rinkes, *Rec. trav. chim.*, **50**, 1127 (1931).

(2) We are indebted to Professor Diels for his courtesy in permitting us to investigate this application of the maleic anhydride reaction.

furans but is hindered by the presence of certain substituents. Crystalline solids were obtained from 2-bromofuran (m. p. 116°), 3-bromofuran (m. p. $131.5-132^{\circ}$), furfuryl methyl ether (m. p. 97°), furfural diacetate (m. p. $126.5-127^{\circ}$), furfurylacetone (m. p. $86-87^{\circ}$) and several others. We have not succeeded in obtaining addition products from compounds containing a carbethoxyl, cyano, nitro or ethylenic group attached directly to the ring.

A study of the effect of hydrolytic agents upon the addition products (substituted 3,6-endoxo- Δ^4 -tetrahydrophthalic anhydrides) has shown that they can be converted directly into the corresponding phthalic acids (or anhydrides).³ Since the orientation of the substituents in the resulting phthalic acids (or anhydrides) is known, this transformation constitutes an absolute method for establishing the position of substituents in the furan ring. Thus, the substituted 3,6-endoxo- Δ^4 -tetrahydrophthalic anhydrides from 2-methylfuran, 2- and 3-bromofuran on heating with hydrogen bromide in glacial acetic acid gave, respectively, 3-methylphthalic anhydride (m. p. $111-113^{\circ}$), 3-bromophthalic anhydride (m. p. $134-135^{\circ}$), and 4-bromophthalic anhydride (m. p. $108-110^{\circ}$). We are now engaged in extending the observations reported here.

(3) Diels and Alder [*Ann.*, **490**, 243 (1931)] have shown that the addition product from furan and maleic acid can be converted into phthalic acid by a series of five reactions, involving four intermediate products.

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VAPOR PRESSURE AND HEAT OF VAPORIZATION OF GRAPHITE

Sir:

A large amount of experimental work has been carried out in the past decade to determine the vapor pressure and heat of vaporization of graphite and very discordant values are given in the literature. We have recently investigated this problem, determining vapor pressure from the rate of loss in weight of carbon rings heated by high frequency induction in a vacuum [reported to April, 1932, Meeting, American Philosophical Society]. The interpretation of the results is complicated by the fact that carbon vapor exists in both monatomic and diatomic forms, the relative amounts being determined by the total pressure and the temperature. Vaughan and Kistiakowsky [*Phys. Rev.*, **40**, 457 (1932)] have independently made calculations, using the equations of quantum statistical mechanics, which support this conclusion.

It is possible to reconcile our results in the temperature range $2350-2800^{\circ}\text{K.}$ with those of Kohn and Gückel [*Z. Physik*, **27**, 305 (1924)] on the vapor pressure of carbon in the arc.

They have taken the value of 4200°K. as the temperature of the positive