$ClO_2$  does not extend above 3750 Å., it was thought that further investigation would prove interesting. It is found that the quantum efficiency at 4360 Å. is only slightly less than that at 3650 Å.  $ClO_2$  does not absorb at 5460 Å. and no photoreaction is obtained on isolating  $ClO_2$  with light of this wave length using a mercury arc and glass filter. On adding a small percentage of bromine a sensitized photoreaction takes place using 5460 Å., the quantum efficiency being practically equal to that at 3650. The equal efficiency of 3650 and 4360 Å. is explicable by the scheme suggested by Schumacher in which predissociation or the activation of  $ClO_2$ molecules leads eventually to the production of  $1ClO + 1ClO_3$  by one quantum of light. Apart from differences in energies of these groups one would expect any chains resulting to be of the same length. The equal quantum efficiency of 5460 Å. could be explained by

$$\begin{array}{rcl} \operatorname{Br}_2 &+ h\nu \longrightarrow \operatorname{Br}_2' \\ \operatorname{Br}_2' &+ \operatorname{ClO}_2 \longrightarrow \operatorname{ClO}_2' &+ \operatorname{Br}_2 \end{array}$$

and then as before. It would be necessary that practically all the activated bromine molecules should be deactivated only by  $ClO_2$  molecules under our conditions.

UNIVERSITY OF SASKATCHEWAN J. W. T. SPINKS SASKATOON, SASK., CANADA RECEIVED DECEMBER 5, 1932 PUBLISHED JANUARY 11, 1933

ROTATORY DISPERSION IN THE VISIBLE AND THE ULTRAVIOLET RANGE OF CONFIGURATIONALLY CORRELATED CARBINOLS, HALIDES AND ACIDS Sir:

High precision dispersion measurements in the visible and in the ultraviolet to about 2300 Å. have been made on the following substances, the configurations of which have been correlated by Levene and Marker.

Compounds	Sign of observed rotation in the visible	Sign of contribution of the functional group	Sign of contribution of the rest of the molecule
2-Methylbutanol	+•	+	-
1-Bromide-2-methylbutane	<u></u> .	+	-
1-Iodo-2-methylnonane		+	-
$\beta$ -Methyl- <i>n</i> -valeric acid		+	

It may be seen from this table that individual substances of this group vary in the direction of their rotation in the visible. An explanation of the differences in the direction of rotations of the correlated substances has been found by the analysis of their rotatory dispersion curves.

The dispersion curves of all these substances may be expressed by the two-term Drude formula

$$[\mathbf{M}] = \frac{a}{\lambda^2 - \lambda_0^2} - \frac{a'}{\lambda^2 - \lambda_0'^2}$$

for rotatory dispersion. In our case the higher  $\lambda_0$  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  $\beta$ -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 furans<sup>1</sup> gives rise to crystalline solids, has led us to investigate this reaction as a general method for the identification of furan derivatives.<sup>2</sup> We have found that addition of maleic anhydride occurs with a variety of substituted

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

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