

the application of heat. The weight of the dry residue obtained in our latest experiments was in one case 77 g. and in the other 78 g. instead of 125 g. reported by the original investigators. In fact, intermittent weighings of the tared evaporation flask during the latter period of the evaporation showed that when its contents weighed 125 g. they were still liquid.

On working up these residues according to the revised procedure of Scheibler we obtained in one case 7 g. (A) and in the other 9 g. (B) of product at the point where ketene acetal should appear. In each of these products the amount of ethyl acetate was determined by saponification of an aliquot with 0.1 *N* potassium hydroxide and the amounts of ethyl alcohol and water were estimated by treatment of an aliquot with phenyl isocyanate followed by the isolation of the phenyl urethan and diphenyl urea. The following summary shows the percentages of these substances which were found to be present in the products which we obtained.

Product	Ethyl acetate, %	Alcohol, % <sup>a</sup>	Water, %	Total % found
A	13.0	72.5	2.2	87.7
B	0	87.5	1.5	89.0

<sup>a</sup> Analyses of a known mixture of alcohol and ethyl acetate, containing 85% of the former and 15% of the latter showed that only 85–90% of the alcohol could be recovered as the phenyl urethan, m. p. 52°.

These results show that the products which we obtained were mainly alcohol containing small amounts of water and ethyl acetate. It is our opinion that the failure of the found values to total 100% is due to the limitations of the procedure used for the determination of alcohol.

On the basis of our experiences, we believe that our failure to prepare ketene acetal is traceable to the discrepancy between the results reported by Scheibler and those obtained by us in connection with the formation of the so-called "primary reaction product" from ethyl acetate and sodium ethoxide. The results which we report now confirm our earlier conclusion that there is not only no evidence for, but definite evidence against, the existence of such a reaction product.

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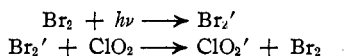
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## BROMINE SENSITIZED PHOTO-DECOMPOSITION OF CHLORINE DIOXIDE

Sir:

Chlorine dioxide is decomposed by light with production of  $\text{Cl}_2\text{O}_6$ , light in the blue and ultraviolet being equally effective [Finkelnburg and Schumacher, *Z. physik. Chem.*, Bodenstein Band, 704 (1931); Spinks, *THIS JOURNAL*, 54, 1689 (1932)]. Since the region of predissociation in

$\text{ClO}_2$  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.  $\text{ClO}_2$  does not absorb at 5460 Å. and no photoreaction is obtained on isolating  $\text{ClO}_2$  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  $\text{ClO}_2$  molecules leads eventually to the production of  $1\text{ClO} + 1\text{ClO}_3$  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



and then as before. It would be necessary that practically all the activated bromine molecules should be deactivated only by  $\text{ClO}_2$  molecules under our conditions.

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### 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	-	+	-
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

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