COMMUNICATIONS TO THE EDITOR

THE QUANTUM YIELD OF CHLOROACETIC ACID HYDROLYSIS

Sir:

Following the report by Rudberg [*Z. Physik*, **24,** 247 (1924)] of a quantum yield of unity for the hydrolysis of monochloroacetic acid in aqueous solution at 2537 Å., this reaction has been employed in a number of cases as an actinometer.

A deviation in the results obtained with the uranyl oxalate and chloroacetic acid actinometers at 2537 Å. has led us to reinvestigate both reactions. A solution 0.01 *M* in uranyl sulfate and 0.05 *M* in oxalic acid gave an average quantum yield of 0.60, in agreement with the value reported by W. G. Leighton and Forbes for this wave length [THIS JOURNAL, **52,** 3139 (1930)]. For a solution 0.5 *M* in monochloroacetic acid, at 25° and an incident intensity of 2×10^{12} to 1×10^{13} quanta/mm.^{2} sec., we find a quantum yield of 0.3 to 0.4 at 2537 Å. This result has been checked on two independent experimental set-ups, using different thermopiles and standard lamps as well as different samples of chloroacetic acid. Amount of hydrolysis was determined in both cases by potentiometric titration of the chloride ion. The results show some variability the source of which has not been located. There seems little doubt, however, but that under our conditions the quantum yield at 2537 Å. is much below unity, and we wish to call this to the attention of any who may be using or considering the use of this reaction as an actinometer.

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LOCATION OF OXYGEN IN CERTAIN STEROIDS

Sir:

In certain compounds of a steroid nature which occur in the adrenal gland there is an atom of oxygen which is exceedingly inert whether in the form of a ketone or of a hydroxyl group [Mason, Hoehn, McKenzie and Kendall, *J. Biol. Chem.*, **120,** 719 (1937)]. Consideration of the possible locations for such an oxygen atom led to the conclusion that it must occupy position 11 or 12 of the steroid nucleus [Kendall, Mason, Hoehn and McKenzie, *Proc. Staff Meet. Mayo Clinic*, **12,** 136, 270 (1937); Steiger and Reichstein, *Helv. Chim. Acta*, **20,** 817 (1937)]. Steiger and Reichstein [*Helv. Chim. Acta*, **21,** 828 (1938)] have recently compared the acid (our acid 1) obtained by oxidation of corticosterone (our compound B) with the 3,11-diketo-Δ^4-*etio*-cholenic acid prepared by degradation of digoxigenin and have found it to be different. They consider that this result casts doubt on position 11 as the location of the oxygen atom in question although it is not conclusive in view of the possible isomerism of the steroid skeleton. We have made a similar comparison with 3,12-diketo-Δ^4-*etio*-cholenic acid and have found that the acid derived from corticosterone differs widely in its properties. This result eliminates the possibility that the oxygen atom in question occupies position 12 of a normal steroid nucleus. The close similarity of the behavior of this oxygen atom with that of the oxygen atom of sarmentogenin which has been assigned to C-11 argues for an identity of position. Degradation of sarmentogenin, which is known to differ from digoxigenin only in the configuration of 1 asymmetric center, probably C-9, should yield a definite answer to this problem.

The degradation of desoxycholic acid to 3,12-diketo-*etio*-cholanic acid has been described [Hoehn and Mason, THIS JOURNAL, **60,** 1493 (1938)]. Bromination in acetic acid solution gave 4-bromo-3,12-diketo-*etio*-cholanic acid, m. p. 197–198° (dec.); $[\alpha]^{25}_{5461} + 109 \pm 2°$. (Calcd. for $C_{20}H_{27}O_4Br$: C, 58.52; H, 6.64; Br, 19.42. Found: C, 58.40; H, 6.65; Br, 19.19.) This bromo acid lost hydrogen bromide when refluxed with pyridine to yield 3,12-diketo-Δ^4-*etio*-cholenic acid, m. p. 205–207°; $[\alpha]^{25}_{5461} +240 \pm 5°$. (Calcd. for $C_{20}H_{26}O_4$: C, 72.68, H, 7.93. Found: C, 72.35; H, 8.24.) Our acid 1 melts at 267–269°; $[\alpha]^{25}_{5461} +291°$. Use of the methyl esters gave better yields and the final product was more readily purified. The ester of the bromo acid melts at 200–201°; $[\alpha]^{25}_{5461} +170 \pm 3°$. (Calcd. for $C_{21}H_{29}O_4Br$: Br, 18.79. Found: Br, 18.94.)