stability may overrule the slight increase in electronegativity found on going from bromine (2.8 on Pauling's scale) to chlorine (3.0), it does not appear capable of surmounting the large increase in electronegativity found in fluorine (4.0).

### Experimental

The benzodifluorochloride used had the following properties: n<sup>24.7</sup>D 1.4622, d<sup>26.2</sup>, 1.2397; molar refractivity calcd. 35.59, found 36.03.

First order rate constants for hydrolysis in 50% (by volume) aqueous acetone, determined as described previously," yielded the following results

- at 36°,  $k = (0.0830 \pm 0.0023) \times 10^{-4} \text{ min.}^{-1}$ at 45°,  $k = (0.2232 \pm 0.0023) \times 10^{-4} \text{ min.}^{-1}$ at 60°,  $k = (0.9880 \pm 0.0048) \times 10^{-4} \text{ min.}^{-1}$ at 30°,  $k = 0.0419 \times 10^{-4} \text{ min.}^{-1}$  (extrapolated from the data above to facilitate comparisons with Table I, reference 3)

The average activation energy was 21.2 kcal./mole.

Acknowledgment.—The authors wish to express their thanks to The Hooker Electrochemical Company for the gift of the benzodifluorochloride used in this investigation.

SCHOOL OF CHEMISTRY

GEORGIA INSTITUTE OF TECHNOLOGY ATLANTA, GEORGIA

# The Determination of the Relative Affinities of a Series of Specific Substrates from their Respective $K_{\rm S}$ and $k_3$ Values<sup>1</sup>

By DAVID S. HOGNESS AND CARL NIEMANN<sup>2</sup> **RECEIVED JANUARY 5, 1952** 

For the systems

$$E_i + S_{ii} \stackrel{k_{1\cdot 1}}{\underset{k_{2\cdot 1}}{\longrightarrow}} ES_1 \stackrel{k_{3\cdot 1}}{\underset{k_{2\cdot 1}}{\longrightarrow}} E_i + P_i \qquad (1.1)$$

$$E_t + S_{2t} \xrightarrow[k_{3,2}]{k_{3,2}} ES_2 \xrightarrow[k_{3,2}]{k_{3,2}} E_t + P_t \qquad (1.2)$$

where  $K_{S_1} = (k_{2.1} + k_{3.1})/k_{1.1}$  and  $K_{S_2} = (k_{2.2} + k_{3.2})/k_{1.2}$  it has been argued<sup>3-5</sup> that  $k_{2.1}/k_{1.1} > k_{2.2}/k_{1.2}$  when  $K_{S_1} > K_{S_2}$  and  $k_{3.1} < k_{3.2}$ , thus implying that in certain cases it is possible to order the relative affinities of a series of specific substrates solely on the basis of their respective  $K_S$  and  $k_3$  values. While this conclusion was at one time accepted by workers in this Laboratory6 it is now recognized that the argument is fallacious and that an unambiguous ordering of affinities cannot be achieved by the above procedure. That this latter conclusion is correct is apparent from the fact that  $k_2/k_1 = K_{\rm S}(1 + k_3/k_2)^{-1}$  and that

$$\frac{k_{2.1}/k_{1.1}}{k_{2.2}/k_{1.2}} = \frac{K_{\rm S1}}{K_{\rm S2}} \left( \frac{1+k_{3.2}/k_{2.2}}{1+k_{3.1}/k_{2.1}} \right) \tag{2}$$

Thus if no restriction is placed upon the values of  $k_{2.1}$  and  $k_{2.2}$ , except that they be positive, then  $k_{2.1}/$  $k_{1.1}$  can be less than, equal to, or greater than  $k_{2.2}/k_{1.2}$  regardless of the relative values of  $K_{S_1}$  and  $K_{S_2}$  and of  $k_{3,1}$  and  $k_{3,2}$ . Since the determination of

(2) To whom inquiries regarding this article should be addressed.

- (4) J. E. Snoke and H. Neurath, Arch. Biochem., 21, 351 (1949).
- (5) J. E. Snoke and H. Neurath, J. Biol. Chem., 181, 789 (1949).
- (6) H. T. Huang and C. Niemann, THIS JOURNAL, 73, 1541 (1951).

CONTRIBUTION NO. 1653 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY CALIFORNIA INSTITUTE OF TECHNOLOGY PASADENA 4, CALIFORNIA

## An Improved Synthesis for $\alpha$ -Methyl- $\Delta, \alpha, \beta$ -butenolide<sup>1,2</sup>

BY WILLIAM H. HOUFF AND HAROLD M SELL **RECEIVED DECEMBER 22, 1951** 

### Introduction

In a study on the effects of inhibition of respiration in germinating seeds by  $\alpha,\beta$ -unsaturated lactones it was necessary to synthesize  $\alpha$ -methyl- $\Delta, \alpha, \beta$ -butenolide. The reported method of synthesis,<sup>8</sup> which involves the condensation of formaldehyde and acetone, could not be employed because of the great tendency for butanol-1-one-3 to polymerize to yield other compounds. This note is a report of a modified method which will produce  $\alpha$ -methyl- $\Delta, \alpha, \beta$ -butenolide in good yields.

#### Experimental

1-Chlorobutanone-3.-Into a 3-necked flask equipped with a dropping funnel, stirrer, and downward condenser was placed 32.5 g. (0.3 mole) of 1-chlorobutanol-3. The solution was heated to 125° and a mixture of 60 g. of potas-sium dichromate in 300 ml. of dilute 1-1 sulfuric acid was added dropwise until the temperature increased and the oxidizing mixture no longer gave the green color of chromous ion. The ketone, as it was formed, was permitted to distil over with the water. The two layers were separated by means of a separatory funnel and the aqueous portion was extracted three times with ether. The product was combined with the ether extracts and the solution was dried over anhydrous sodium sulfate for 12 hours. The ether was dis-tilled off and the fraction distilling at  $52-53^{\circ}$  at 15 mm. was collected. The yield was 24 g. or 80%.  $\alpha$ -Hydroxy- $\alpha$ -methylbutyrolactone.—To 24 g. (0.22 mole) of 1 observe that 100 methylbutyrolactone.

of 1-chlorobutanone-3 in 100 ml. of water was added 100 ml. of a solution containing 20 g. of potassium cyanide. The solution was cooled to  $15^{\circ}$  and the 100 ml. of a 25%solution of hydrochloric acid was added slowly with stirring. An additional quantity of 200 ml. of concentrated hydrochloric acid was added and the solution stirred vigorously for four hours. The reaction mixture was extracted continuously with ether in a liquid-liquid extraction unit for eight hours. After drying the ethereal extract over anhydrous sodium sulfate, the ether was removed under vacuum. drous sodium sulfate, the ether was removed under vacuum. The crude product distilled with an evolution of hydrogen chloride. The yield of the fraction distilling at 109–110° at 6 mm. was 14 g. or 54%; m.p. of the *p*-nitrobenzoate of the hydroxylactone 161–161.5°, reported<sup>8</sup> m.p. 162°.  $\alpha$ -Methyl- $\Delta,\alpha,\beta$ -butenolide.—The same procedure de-scribed by Cavallito, *et al.*,<sup>3</sup> was used. The product dis-tilling at 82° at 7 mm. was collected. The yield was 3.5  $\alpha$  or 30%:  $\pi^{30}$  was 1465

g. or 30%; n<sup>20</sup>D was 1.465.

DEPARTMENT OF AGRICULTURAL CHEMISTRY

MICHIGAN STATE COLLEGE

EAST LANSING, MICHIGAN

<sup>(1)</sup> Supported in part by a grant from Eli Lilly and Company.

<sup>(3)</sup> H. Neurath and G. W. Schwert, Chem. Revs., 46, 69 (1950).

<sup>(1)</sup> Published as Journal Article No. 1308 of the Michigan Agricultural Experiment Station.

<sup>(2)</sup> The research was supported by a grant from the Rockefeller Foundation,

<sup>(3)</sup> C. J. Cavailito and T. H. Haskell, THIS JOURNAL, 68, 2332 (1946).