β-Bromo-α-chloro-β-formylacrylic Acid

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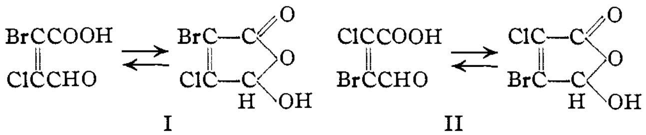
The method described by Simonis[1] of treating furfural with an excess of bromine in aqueous solution to obtain mucobromic acid is useful for the preparation of small quantities of that compound for laboratory purposes. On a larger scale, however, this procedure is inconvenient not only because of the large quantity of bromine used, but also because it has to be added all at once in spite of the exothermic character of the reaction. To arrive at a practical procedure for larger quantities we tried using an amount of bromine just in excess of the one-mole equivalent that appears in the final compound and then employing chlorine to regenerate bromine from the hydrobromic acid formed in the course of the reaction, thus making it available for further bromination of furfural.

In carrying out this procedure we obtained in almost quantitative yield, not the expected mucobromic acid, but a compound with similar properties and a molecular weight of 213, microanalysis of which showed it to be a bromochloroformylacrylic acid.

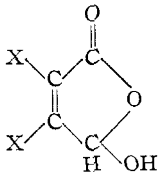
An acid of the same empirical formula had been obtained previously by Hill[2] in very small quantity in a tedious way. Starting with ethyl tetrachlorotetrahydrofuroate, he obtained 4,5-dichlorofuroic acid from a fraction of the pyrogenically decomposed ester.[3] By reducing this compound to 4-chlorofuroic acid and oxidizing the latter with bromine in aqueous solution, he obtained what he called mucochlorobromic acid and assigned to it the formula of α-bromo-β-chloro-β-formylacrylic acid (I).



I II

Using this procedure of Hill, we obtained only traces of his acid until we followed the advice of Vander Wal[4] to use 3,4-dichloro-2-furoic acid instead of 4,5-dichloro-2-furoic acid to make 4-chloro-2-furoic acid. It was then an easy task to obtain reasonable quantities of I and to compare it with the acid formed in our reaction. It was essential to have more material than could be obtained by Hill's procedure because the melting and mixed melting point did not serve to distinguish or to identify the two products. The infrared absorption spectra, however, showed that the two acids are different compounds and indicated that we had obtained β-bromo-α-chloro-β-formylacrylic acid (II).

The infrared spectra of mucochloric and mucobromic acids, which were included for comparison, show clearly that each exists, not as an open chain formylacrylic acid, but in the form of a ring as



Neither acid shows any acid carbonyl absorption around 1700 cm.$^{-1}$ but rather each has carbonyl absorptions characteristic of strained ring carbonyls; mucobromic acid a singlet at 1767 cm.$^{-1}$ and mucochloric acid a doublet at 1770 and 1782 cm.$^{-1}$ (see Fig. 3). Neither acid shows any aldehyde absorption around 1690 cm.$^{-1}$. Furthermore, the hydroxyl absorptions at 3300 cm.$^{-1}$ for mucobromic acid and at 3312 cm.$^{-1}$ for mucochloric acid are of too high frequency to be hydroxyl absorptions of carboxyl groupings which absorb at about 3100 cm.$^{-1}$. The hydroxyl absorptions of these two compounds are correct, however, for alcoholic –CHOH absorptions (see Fig. 1).

Likewise the infrared spectra of I and II show that each exists entirely in the same ring structure as mucochloric and mucobromic acids, since the spectrum of each shows strained ring carbonyl and alcoholic –CHOH absorptions and no carboxyl carbonyl or carboxyl hydroxyl absorptions. The infrared spectra of I and II are similar enough to indicate clearly that they both have the same ring structure, but their spectra are sufficiently different to show that they are not identical compounds. The fact that II and mucochloric acid both have a carbonyl doublet with identical absorptions at 1770 and 1782 cm.$^{-1}$ shows that the environment of the carbonyl group is the same in the two cases. Moreover, both I and mucobromic acid have a single carbonyl absorption at 1774 cm.$^{-1}$ in the former and at 1767 cm.$^{-1}$ in the latter. This infrared evidence shows that I is β-chloro-α-bromo-β-formylacrylic acid and that II is the β-bromo-α-chloro derivative.

In chemical respects, too, the new acid shows quite significant differences when compared with I. If II, for example, reacts with sodium nitrite, the yield of nitromalonic aldehyde is much larger than from I and equals exactly the yield obtained from mucobromic acid under the same conditions. In this connection it should be mentioned that from mucochloric acid only very small quantities of nitromalonic aldehyde are formed.

The mechanism of the reaction leading to II is not quite clear. The over-all equation according to which it takes place is

$$2C_5H_4O_2 + Br_2 + 9Cl_2 + 6H_2O \longrightarrow 2C_4H_2O_3BrCl + 16HCl + 2CO_2$$

During the first stages, at least, the conditions for the formation of mucobromic acid prevail, but no trace of a dibromo acid is ever found in the final product. It is, therefore, reasonable to conclude that, at some stage of the oxidation, there is an exchange of one bromine atom for chlorine, a phenomenon similar to that already observed by Hill in

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(1) H. Simonis, *Ber.*, **32**, 2084 (1899).

(2) H. B. Hill and J. Torrey, Jr., *Am. Chem. J.*, **22**, 89 (1899).

(3) Hill claimed erroneously that this acid was 3,5-dichlorofuroic acid. Vander Wal (ref. 4) proved it to be 4,5-dichlorofuroic acid which by reduction yields 4-chloro-2-furoic acid not, as Hill claimed, 3-chloro-2-furoic acid.

(4) R. J. Vander Wal, *Iowa State College J. Sci.*, **11**, 128 (1936).

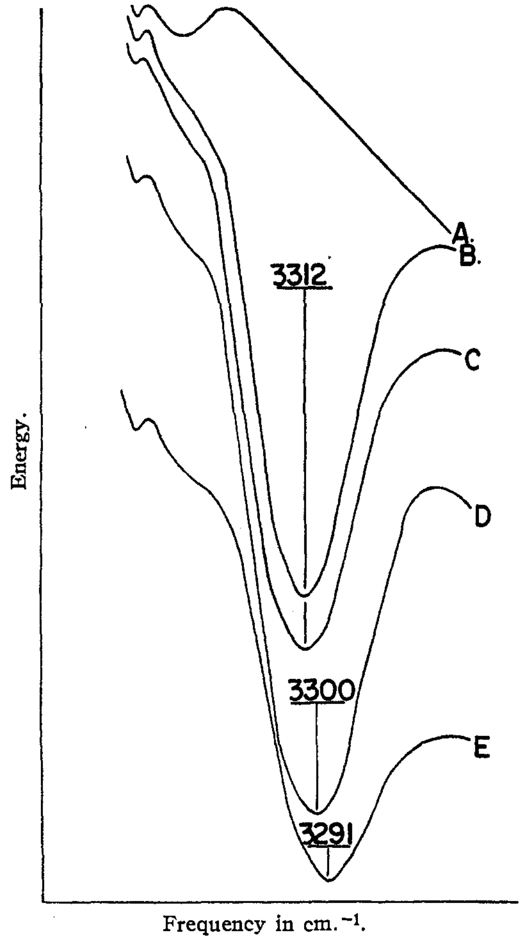

Fig. 1.—A, radiation curve; B, mucochloric acid; C, β-bromo-α-chloro-β-formylacrylic acid; D, mucobromic acid; E, α-bromo-β-chloro-β-formylacrylic acid.

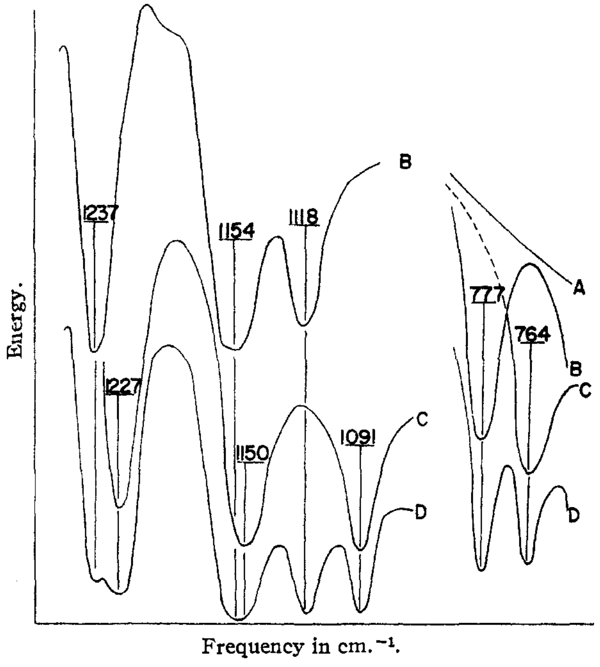

Fig. 2.—A, radiation curve; B, mucochloric acid; C, mucobromic acid; D, mixture, mucochloric and mucobromic acids.

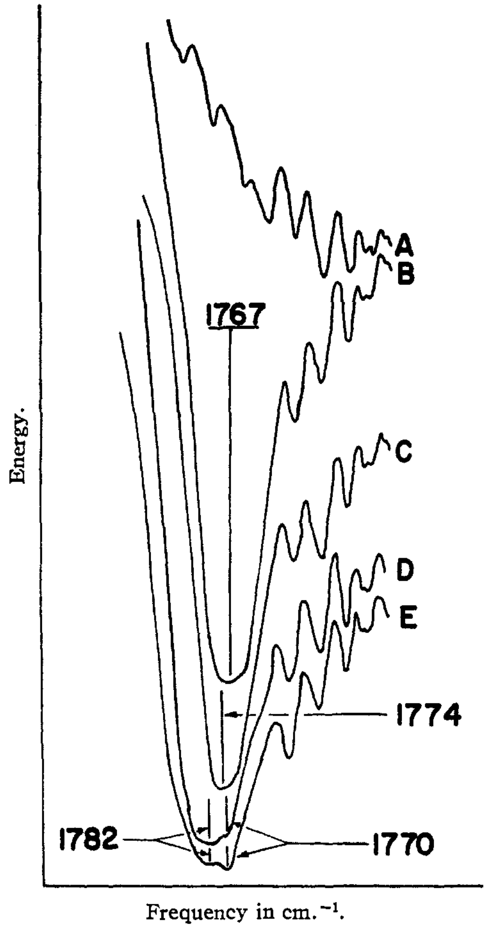

Fig. 3.—A, radiation curve; B, mucobromic acid; C, α-bromo-β-chloro-β-formylacrylic acid; D, mucochloric acid; E, β-bromo-α-chloro-β-formylacrylic acid.

the dibromocrotonolactones.[5] However, when mucobromic acid was treated with chlorine in hydrochloric acid solution at elevated temperatures, no mucobromochloric acid or bromine was obtained.

Though it was not probable, because of the invariable ratio of bromine and chlorine in our final product, that it consisted of a mixture of mucochloric and mucobromic acids, we recrystallized a molar mixture of both acids from benzene. We actually obtained crystals of the same shape and almost the same α and β refractive indices. The infrared absorption curve, however, indicated clearly that this was a mixture and chemically not unique. In Fig. 2 covering the absorption region of 750–1250 cm.$^{-1}$ frequency, it is shown that the absorption of the mixture is simply the sum of the absorptions of the two components.

Experimental

β-Bromo-α-chloro-β-formylacrylic Acid.—The reaction was run in a round-bottom flask with five necks fitted with an efficient agitator, a long reflux condenser, a dropping funnel with a capillary stem, a subsurface gas feed tube and a thermometer. It is essential that the capillary of the dropping funnel always remains below the surface of the reaction mixture and that the flow of the furfural never stops, otherwise the furfural turns into tar.

The flask was charged with 150 g. of 48% hydrobromic acid, 175 ml. of water and 72 g. of bromine. The bromine

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[5] H. B. Hill and R. N. Cornelison, *Proc. Am. Acad. of Arts and Sciences*, **XXIX**, 89 (1899).

dissolved completely in the liquid, forming a complex which could be heated above the boiling point of bromine. The excess of bromine (including that contained in the hydrobromic acid) is necessary because a certain loss of bromine is unavoidable on a laboratory scale. It is carried away by the rapid current of hydrochloric acid (and CO_2) formed in the reaction.

The contents of the flask was heated to 65° and 96 g. of furfural added at such a rate that the steady flow through the capillary took about 2 to 2.5 hours. The furfural reacts exothermically with the bromine. The temperature was allowed to reach 75° and the bromine started to reflux. As soon as the deep red color of the liquid became lighter, a fast current of chlorine was passed through the liquid. The flow of furfural and chlorine has to be adjusted in a ratio of 1:3 by weight. The temperature was kept between 75 and 85° by external cooling. When about $^2/_5$ of the furfural had been added, the evolution of large quantities of hydrogen chloride began. Almost no cooling was then needed to keep the temperature at 80–85°. After all of the furfural was in, the temperature was raised to 95° and the chlorine flow cut in half. Chlorine was then added until the whole usage was about 290 g. (90–94% of the theoretical 4.5 mole equivalents). There remained in the flask a pale yellow liquid which on cooling formed a stiff slurry of almost white crystals. This crude product was purified by crystallization from hot water. The yield was 90–94% of theory; m.p. of the purified compound, 122.5°. Titration with caustic showed a molecular weight of 212 (theory, 213).

Anal. Calcd. for $C_4H_2O_3BrCl$: C, 22.5; H, 0.95; Br + Cl, 54.07. Found: C, 22.7; H, 1.02; Br + Cl, 53.7.

Acknowledgments.—We are indebted to Dr. R. J. Vander Wal for suggesting the use of 3,4-dichloro-2-furoic acid to make Hill's 4-chloro-2-furoic acid and for his kindness in supplying a copy of his thesis. We wish to thank Dr. D. N. Kendall for making and interpreting the infrared absorption curves, and O. E. Sundberg for the microanalysis.

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Kinetics of the Hydrolysis of *p*-Nitrosodimethylaniline[1]

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The cleavage of *p*-nitrosodialkylanilines by base, a classical preparative method for dialkylamines, has often been considered to be a typical aromatic nucleophilic displacement reaction.[2] There has been, however, beyond gross similarities, no available evidence to support this contention. Further, since this is one of the few known examples of a reaction in which the group displaced is activated by a nitroso group, it was of interest to examine the reaction kinetically.

$$p\text{-ON—C}_6\text{H}_4\text{N(CH}_3)_2 + \text{NaOH} \longrightarrow p\text{-ON—C}_6\text{H}_4\text{ONa} + (\text{CH}_3)_2\text{NH}$$

Experimental

Materials.—*p*-Nitrosodimethylaniline was prepared by nitrosation of dimethylaniline,[3] and obtained as green crystals from ligroin with a melting point of 86°.[4] *p*-Nitrosophenol was obtained by hydrolysis of the nitrosoaniline,[5] and purified by recrystallization from water to a constant melting point of 124–128°.[6]

Method.—It was found from the absorption spectra of *p*-nitrosodimethylaniline in 50% alcohol–water and of *p*-nitrosophenol in the same solvent, which was also approximately 0.2 *M* in sodium hydroxide, that at a wave length of 675 mμ there is a maximum absorption due to *p*-nitrosodimethylaniline and a corresponding minimum in the curve for *p*-nitrosophenol. Using a Coleman spectrophotometer, the optical densities of various mixtures of *p*-nitrosodimethylaniline and *p*-nitrosophenol were determined, and a standard curve drawn.

One-tenth molar solutions of *p*-nitrosodimethylaniline in 50% alcohol–water were prepared frequently by weighing out the calculated amount of the substance. In carrying out an experimental run, definite quantities of this 0.100 *M* *p*-nitrosodimethylaniline solution were measured into the reaction flask by means of a buret. A calculated amount of potassium chloride was added to maintain a constant ionic strength of 0.203. The flask and contents were allowed to reach bath temperature and a calculated quantity of standard sodium hydroxide, also at bath temperature, added with stirring from a pipet. At convenient intervals samples of the reaction mixture were withdrawn by means of a pipet and diluted to give a concentration of approximately 0.01 *M* or less. The extent of dilution nearly stopped the reaction. The diluted samples were immediately transferred to the spectrophotometer cuvettes and readings of the optical density taken at 675 mμ. The concentrations of *p*-nitrosodimethylaniline were then determined from the standard curve, and the concentration of the withdrawn sample calculated using the appropriate dilution factor. Runs were made at 30 and 50 ± 0.05°.

Results and Discussion

Typical data for reactions at 30 and 50° are listed in Tables I and II, respectively, and plots of these data are given in Fig. 1. The results of several runs at various concentrations are given in Tables III and IV. From the average values of the rate constants at the two temperatures the energy of activation was calculated to be 13 kcal. and log *PZ* to be 6.

TABLE I

TYPICAL DATA FOR A REACTION AT 30°

Time, sec.	Optical density	$(b - x)$ (p-ONC$_6$H$_4$N(CH$_3$)$_2$)	$(a - x)$ (NaOH)	$\log \frac{a-x}{b-x}$
0	...	0.0750	0.203	0.432
360	0.511	.0599	.188	.497
615	.495	.0572	.185	.510
1065	.471	.0535	.181	.529
1515	.460	.0517	.180	.542
1810	.450	.0505	.178	.548
2340	.430	.0476	.176	.568
2595	.420	.0455	.173	.580

TABLE II

TYPICAL DATA FOR A REACTION AT 50°

Time, sec.	Optical density	$(b - x)$ (p-ONC$_6$H$_4$N(CH$_3$)$_2$)	$(a - x)$ (NaOH)	$\log \frac{a-x}{b-x}$
0	...	0.0500	0.199	0.600
135	0.520	.0413	.190	.663
380	.479	.0365	.186	.707
610	.440	.0325	.182	.748
945	.400	.0282	.177	.798
1880	.310	.0187	.168	.954

The second-order character of the rate constants, and the values of the Arrhenius parameters are in

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[1] Abstracted from the thesis presented by M. L. Adams to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Master of Science.

[2] (a) A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 377; (b) W. A. Waters, "Physical Aspects of Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1950, p. 497; (c) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

[3] W. J. Hickenbottom, "Reactions of Organic Compounds," Longmans, Green and Co., New York, N. Y., 1936, p. 287.

[4] C. Wurster and L. Roser, *Ber.*, **12**, 1823 (1879).

[5] E. ter Meer, *ibid.*, **8**, 623 (1875).

[6] E. Bamberger, *ibid.*, **33**, 1955 (1900).