61. *Electrophilic Substitution. Part VIII.* The Nitration of Dibenzofuran and a New Method of Ultraviolet Spectrophotometric Analysis of Mixtures.*

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Dibenzofuran has been nitrated with nitric acid in acetic anhydride. The proportions of isomers produced have been measured spectrophotometrically and shown to be : 1-, 20% ; 2-, 40% ; 3-, 40%. The presence of the 1-isomer as a product of nitration is established for the first time.

A new method of ultraviolet spectrophotometric analysis of mixtures is described.

DIBENZOFURAN was nitrated by Borsche and Booth [1] using a three-fold excess of fuming nitric acid in acetic acid ; the main product was 3-nitrodibenzofuran. From the mother-liquors Borsche and Schake [2] obtained a second compound (m. p. about 110°), which they thought to be 2-nitrodibenzofuran. Gilman, Bywater, and Parker [3] showed this to be a mixture containing 2-nitrodibenzofuran, which they synthesised. Ryan, Keane, and M'Gahan,[4] and later Cullinane [5] and Ryan,[6] used also other media, *e.g.*, carbon tetrachloride, and confirmed that the main isomer was the 3-nitrodibenzofuran.

Yamasiro [7] repeated Borsche and Schake's work and claimed to detect in the mixture traces of the 1-isomer (m. p. about 110°). Gilman and Swiss [8] have synthesised the 1-isomer and shown it to be somewhat different from Yamasiro's compound. We have measured the spectrum of Gilman's 1-nitro-isomer and it does not agree with that recorded by Yamasiro, even qualitatively.

The previous work seems to point to an isomer distribution : 1(?)-, 1—5% ; 2-, 20% ; 3-, 70%.

We have nitrated dibenzofuran in acetic anhydride at 4° and 25° under conditions such that only partial nitration took place (maximum conversion 15%). The resulting mixture was chromatographed on alumina to free the nitro-compounds from excess of dibenzofuran. Spectrophotometric analysis by a method described below showed the isomer distribution (see Table) to be about : 1-, 20% ; 2-, 40% ; 3-, 40%.

Temp.	Nitro-product (g.)	Nitration (%) *	Proportion of isomers 1-	2-	3-
4°	0·043	2	25	39	36
25	0·302	15	19	40	41
25	0·019	4	22	41	37

* With respect to HNO_3 used.

The 3-isomer was prepared by Borsche and Booth's method and from it the 2-isomer was prepared as described by Gilman. The spectra of the three isomers were measured in alcohol and used as standards for the analysis.

The following method of analysing the spectroscopic results has been devised. It enables the whole ultraviolet spectrum to be taken into consideration, rather than measurements at isolated wavelengths and consequently it gives much more reliable results than conventional methods. Although the method is most convenient for two-component systems, it can be extended to more complex cases ; traces of impurities are readily detected.

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* Part VII, preceding paper.

[1] Borsche and Booth, *Ber.*, 1908, **41**, 1940.

[2] Borsche and Schake, *Ber.*, 1923, **56**, 2500.

[3] Gilman, Bywater, and Parker, *J. Amer. Chem. Soc.*, 1935, **57**, 885.

[4] Ryan, Keane, and M'Gahon, *Proc. Roy. Irish Acad.*, 1927, **37**, 368.

[5] Cullinane, *J.*, 1930, 2268.

[6] Cullinane and Ryan, *Sci. Proc. Roy. Dublin Soc.*, 1924, *A*, **17**, 321.

[7] Yamasiro, *Bull Chem. Soc. Japan*, 1941, **16**, 61.

[8] Gilman and Swiss, *J. Amer. Chem. Soc.*, 1944, **66**, 1884.

Consider a solution containing substances 1, 2, 3 . . . *i* at known concentrations x_1, x_2, x_3, . . . x_i g. per l.

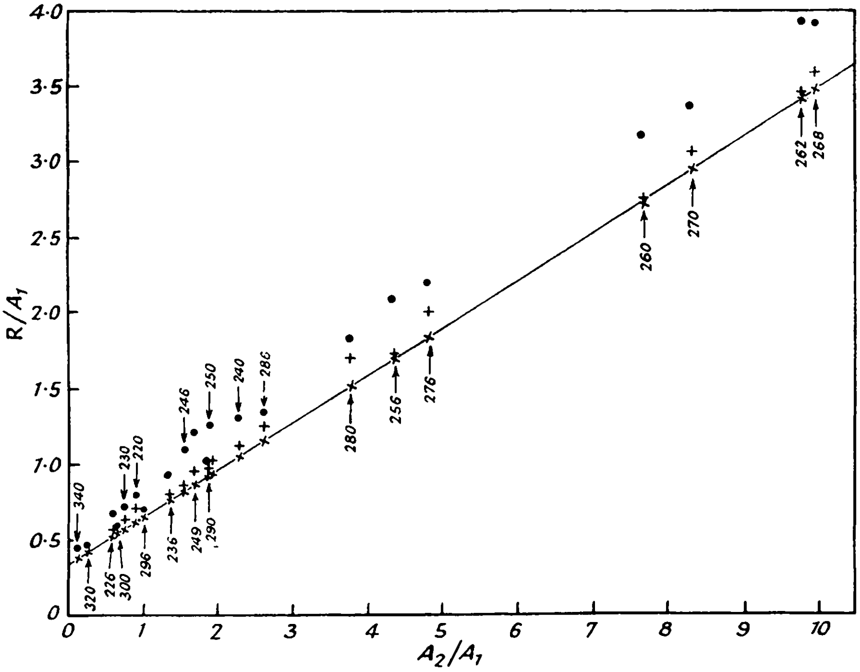
Standard solutions of 1, 2, 3 . . . *i* have known concentrations, c_1, c_2, c_3, . . . c_i g. per l. and give rise to absorptions (measured as $\log_{10} I_0/I$) of A_1, A_2, A_3, . . . A_i at wavelength λ.

Thus if R is the observed value of $\log_{10} I_0/I$ for the unknown solution, and if Beer's law is obeyed, then :

$$\mathrm{R} = \frac{x_1}{c_1}A_1 + \frac{x_2}{c_2}A_2 + \frac{x_3}{c_3}A_3 + \quad \ldots . \frac{x_i}{c_i}A_i \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where all measurements refer to the same value for λ.

Plot of R/A_1 *against* A_1/A_2, *where subscripts* 1 *and* 2 *refer to* 3- *and* 2-*nitrobenzofuran respectively. The numerals for each point refer to the wavelength at which that ratio was obtained.*



● Original value. + Corr. for 1-nitrobenzofuran. × Corr. for 1-nitrobenzofuran and benzofuran.

Dividing throughout by A_1 gives :

$$\frac{\mathrm{R}}{A_1} = \frac{x_1}{c_1} + \frac{x_2}{c_2}\cdot\frac{A_2}{A_1} + \frac{x_3}{c_3}\cdot\frac{A_3}{A_1} + \quad \ldots . \frac{x_i}{c_i}\cdot\frac{A_i}{A_1} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

Consider a two-component system. R, A_1, A_2, c_1, and c_2 are known experimentally. If the values of R/A_1 for various wavelengths are plotted against the corresponding values of A_2/A_1 the points should lie on a straight line of slope x_2/c_2; and the intercept on the R/A_1 axis gives x_1/c_1. Any deviations from a straight line indicate the presence of other components.

In the case of a mixture containing *n* components ($n > 2$), a plot of $(\mathrm{R}/A_1 - \sum_{i \geq 3}^{n} x_i A_i/c_i A_1)$ against A_2/A_1 will give a straight line. Here $A_i/c_i A_1$ is known; the appropriate values of x_i can be found by trial and error. This can in practice be done very easily and at any stage the presence of additional components can be deduced at once.

The procedure is illustrated by the Figure which refers to the nitration product from dibenzofuran. The first set of points (●) shows the plot of R/A_1 against A_2/A_1, where A_1 and A_2 are, respectively, for 3- and 2-nitrodibenzofuran. The curvature of the plot indicates that other components were present. The second set of points (+) was obtained after allowance for the presence of the 1-isomer; the plot is still not quite linear. Further trials showed that the fourth compound was dibenzofuran itself. The third set of points (×), corresponding to the mixture indicated above together with 2% of dibenzofuran, lie accurately on a straight line.

EXPERIMENTAL

3-*Nitrodibenzofuran*.—Prepared by Borsche and Booth's method,[1] recrystallised three times from alcohol, and sublimed *in vacuo*, this had m. p. 181·5—182·5°.

2-*Nitrodibenzofuran*.—3-Nitrodibenzofuran was reduced to 3-aminodibenzofuran by Dewar and Mole's method.[9] An ethereal solution of amine was obtained from which the hydrochloride was precipitated in 90% yield. This was then used in the preparation of 2-nitrodibenzofuran as described by Gilman.[10] The product, recrystallised twice from alcohol and sublimed *in vacuo*, had m. p. 150·5—151·5°.

2-*Aminodibenzofuran*.—This was prepared by the same method in 90% yield and had m. p. 125—126.

Spectra.—The following absorption bands (mμ) and intensities (log E in parentheses) were measured in 95% alcohol on a Unicam S.P. 500 ultraviolet spectrophotometer :

3-Nitro : $\lambda_{\text{max.}}$ 322 (4·233)
$\lambda_{\text{min.}}$ 264 (3·358)

2-Nitro : $\lambda_{\text{max.}}$ 286 (4·213), 266 (4·426), 241 (4·334), 213 (3·383)
$\lambda_{\text{min.}}$ 284 (4·210), 247 (4·074), 228 (4·064)

1-Nitro : $\lambda_{\text{max.}}$ 336 (3·920) 244 (4·100),210 (4·650)
$\lambda_{\text{min.}}$ 289 (3·431), 233 (4·088)

Nitration of Dibenzofuran.—Separate experiments were conducted at 4° and 25°. Nitric acid (0·42 ml.; *d* 1·5; 0·01 mol.) in acetic anhydride (100 ml.) was added to a stirred solution of dibenzofuran (1·68 g., 0·01 mol.) in acetic anhydride (300 ml.). After 30 hr. the anhydride was hydrolysed with ice-water (1 l.), and the product isolated with chloroform and then chromatographed four times from benzene on alumina (Peter Spence type " H "; 20 × 3·5 cm.). Dibenzofuran was eluted first, and the following homogeneous yellow band of mononitrodibenzofurans was then washed off with chloroform. The first column left a few mg. of red material, probably oxidation products. The mixture of nitro-compounds was analysed by the method described above.

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[9] Dewar and Mole, *J.*, 1956, 2556.

[10] Gilman, Brown, Bywater, and Kirkpatrick, *J. Amer. Chem. Soc.*, 1934, **56**, 2473.