

CVIII.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part XIII.*

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IN the previous communication (J., 1926, 1248), it was shown that the dihalogen derivatives of a series of barbituric acids are reduced by hydrazine hydrate to the corresponding monohalogen compounds, and spectroscopic evidence was submitted which indicated that barbituric acid and its monohalogen derivatives exist in the enolic modification, whereas the dihalogen derivatives possess a definitely ketonic structure. Further support for this view has now been found in the absorption spectra of 1-phenylbarbituric acid and 1:3-diphenylbarbituric acid and their derivatives, the graphs for which are shown in Figs. 1—4. The parent acids and the monohalogen derivatives give absorption spectra showing well-defined bands characteristic of the enolic modification; the dihalogen compounds, on the other hand, show general absorption only.

Comparison of the various graphs shows that the spectra of the phenylbarbituric acids are of a much simpler character than the absorption spectrum of barbituric acid itself, the complex bands in the latter being replaced by a principal band extending over $1/\lambda$ 3700—4200. That this band is characteristic of the enolic modification is evident from the fact that it occurs in the presence of alkali,

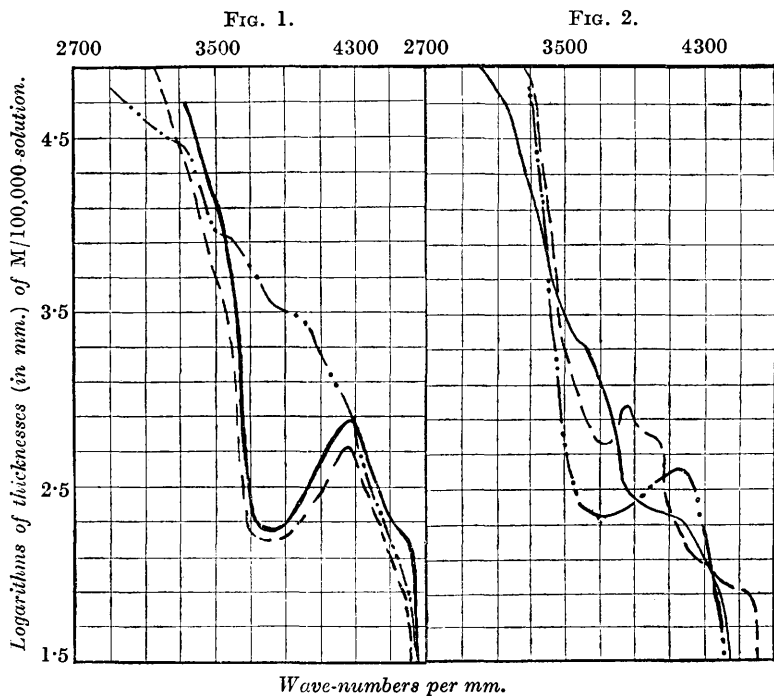


FIG. 1.

————— 1-Phenylbarbituric acid (in water).
 - - - - - " + NaOH.
 - · - · - · " + HCl.

FIG. 2.

————— 5:5-Dibromo-1-phenylbarbituric acid (in alcohol).
 - - - - - " + NaOEt.
 - · - · - · 5-Bromo-1-phenylbarbituric acid (in water).

and virtually disappears in the presence of hydrochloric acid; and since the band is only slightly more persistent in an alkaline solution than in an aqueous solution of the parent acids or their monohalogen derivatives, the latter also must exist in the enolic form.

The spectra of the dihalogen compounds (Figs. 2 and 4) undergo a marked change on the addition of alkali, the band characteristic

of the enolic modification developing to some extent. The decomposition of the dihalogen compound to the corresponding monohalogen derivative in alkaline solution is thus indicated, and additional proof of such change is given below.

For the purpose of comparison, the work was extended to the examination of absorption spectra of typical thiobarbituric acids,

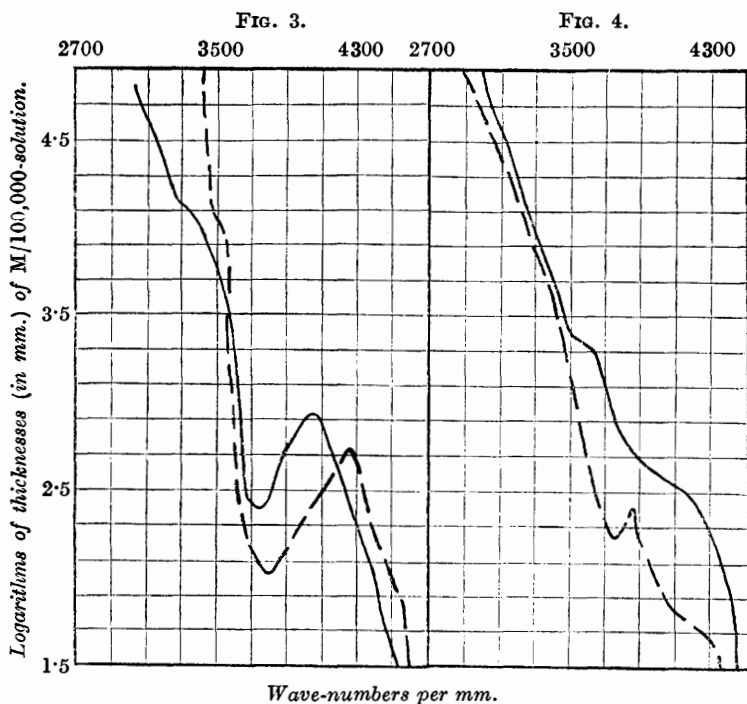


FIG. 3.

————— 1:3-Diphenylbarbituric acid (in alcohol).
 - - - - - " " + NaOEt.

FIG. 4.

————— 5:5-Dibromo-1:3-diphenylbarbituric acid (in alcohol).
 - - - - - " " + NaOEt.

and the results obtained with 2-thiobarbituric acid and 2-thio-1:3-diphenylbarbituric acid are shown in Figs. 5 and 6. The spectrum of the former presents a series of bands similar to those given by barbituric acid, whereas the diphenyl thio-analogue shows the simplification of absorption due, as already recorded, to the introduction of phenyl radicals. In the spectra of the thio-acids, however, the bands are all moved towards the visible region, as the

following values show. In 2-thio-1:3-diphenylbarbituric acid, the band of frequency $1/\lambda$ 3460 approximately corresponds with the band $1/\lambda$ 3760 of 1:3-diphenylbarbituric acid, and the bands of 2-thiobarbituric acid with approximate frequencies $1/\lambda$ 2980,

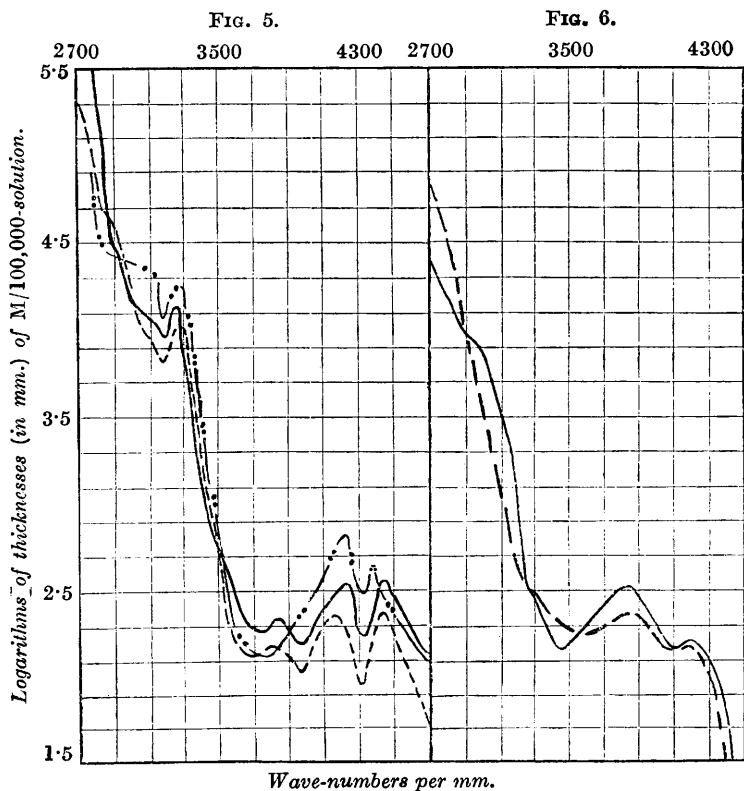


FIG. 5.

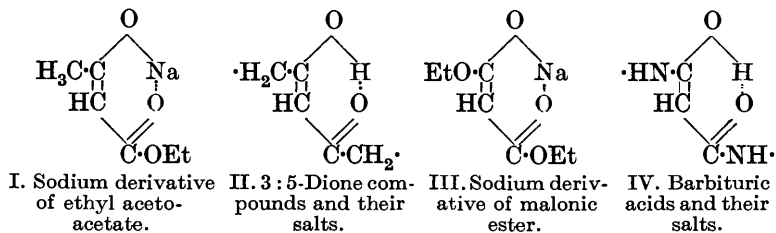
————— 2-Thiobarbituric acid (in water).
 - - - - - " + NaOH.
 - · - · - · - " + HCl.

FIG. 6.

————— 2-Thio-1:3-diphenylbarbituric acid (in alcohol).
 - - - - - " + NaOEt.

3550, 3760, 4120 correspond with those at $1/\lambda$ 3180, 3750, 3900, 4500 approximately in the absorption spectrum of barbituric acid. It would further appear that the enolic modifications of the thio-acids are very stable, as but little change takes place in the character of the absorption in the presence of acid.

Hartley (J., 1905, **87**, 1796) reported that barbituric acid transmitted a continuous spectrum through thicknesses of $M/1000$ -solution up to 20 mm. This statement is surprising, as it has been found (Brannigan, Macbeth, and Stewart, J., 1913, **103**, 406) that the sodium derivatives of malonic esters, like the metallic derivatives of ethyl acetoacetate (Baly and Desch, J., 1904, **85**, 1029; 1905, **87**, 766; Hantzsch, *Ber.*, 1910, **43**, 3049), are characterised by a deep band, and further, that 1 : 1-dimethylcyclohexane- and cyclohexanespirocyclohexane-3 : 5-diones and their monohalogen derivatives show (Graham and Macbeth, J., 1922, **121**, 2601) strong selective absorptions which are practically identical with the absorptions of their respective sodium salts. The hypothesis proposed (Hantzsch, *loc. cit.*; Graham and Macbeth, *loc. cit.*) to account for the selective effects in these cases is also applicable to the salts of the barbituric acids and their monohalogen derivatives, and to the acids themselves if strongly ionised, for the same type of six-membered "ring" may be produced in all cases by the formation of an internal salt calling into play auxiliary valencies of the metallic (or hydrogen) atom. It was therefore of interest to find that the apparently exceptional behaviour of the barbituric acids was due to an incorrect observation.



Trubsbach (*Z. physikal. Chem.*, 1895, **16**, 711) and Hantzsch (*Ber.*, 1902, **35**, 1006) traced the acidity of barbituric acid to enolisation involving the methylene group, and Wood and Anderson (J., 1906, **89**, 1831) supported this view by showing the almost negligible values of the dissociation constants of C -dialkyl barbituric acids compared with the value for the parent compound. It was thought that a series of conductivity measurements would afford confirmatory evidence of the enolic constitutions of the barbituric acids and their monohalogen derivatives and of the existence of the dihalogen compounds in ketonic forms. The method was applied to such substances and also to a series of derivatives of 1 : 1-dimethylcyclohexane- and cyclohexanespirocyclohexane-3 : 5-diones. Approximate measurements of the hydrogen-ion concentrations of the solutions were in some cases made by the capillator method.

TABLE I.

	<i>M</i> /100 in 80% alcohol.		<i>M</i> /200 in 40% alcohol.	
	<i>A.</i>		<i>A.</i>	<i>B.</i>
<i>1 : 1-Dimethylcyclohexane-3 : 5-dione and derivatives.</i>				
Parent	0·3884		2·792	3·8
4-Bromo-derivative	2·3017		22·590	2·9
4-Chloro-derivative	2·3400		21·310	2·8
4 : 4-Dichloro-derivative	0·1501		0·976	4·2
4 : 4-Dibromo-derivative	0·1694		1·222	4·1
4-Chloro-4-bromo-derivative	0·1953		1·728	4·0
<i>cycloHexanespirocyclohexane-3 : 5-dione and derivatives.</i>				
Parent	0·4602		2·341	3·9
4-Bromo-derivative	2·3173		21·730	2·8
4 : 4-Dichloro-derivative	0·2148		0·9615	4·2

Columns *A* give the molecular conductivities at 25°, column *B* gives the hydrogen-ion concentrations.

The conductivity measurements were made with unplatinised electrodes. The figures for the molecular conductivities of the dihalogen compounds are not absolute, but maximum, values. This is due to the partial reduction of these compounds to the monohalogen compounds, which occurs on keeping. Direct tests showed that oxidation of the alcohol to aldehyde occurs with the formation of free halogen acid. The change is surprisingly rapid in the presence of platinised electrodes, and it was found possible to reduce the error to a minimum only by using unplatinised electrodes and determining the conductivity as rapidly as possible after making the solution. It is impossible to eliminate the error altogether, as the initial increase in conductivity is very rapid, and the values for the dihalogen compounds are so small that the formation of even traces of the halogen acid and monohalogen compound causes a very considerable percentage increase in the value. A typical effect of the decomposition on the conductivity values is seen in Table II, where the "molecular conductivity" (*P*) is the value

$$P = scx/R(1000 - x),$$

s being the cell constant, *c* the number of c.c. containing 1 g.-mol. of substance, *R* the resistance balanced against the resistance of the cell, and *x* the balancing length on a 1000-cm. bridge.

The values in Table I show that whereas the introduction of a single halogen atom in the 4-methylene group increases the molecular conductivity considerably, the substitution of halogen for the remaining hydrogen causes a decrease to a value considerably smaller than that of the parent compound; moreover, for the reasons stated, the experimental values for the dihalogen compounds must be considerably greater than the absolute values. It must be inferred, therefore, that whilst in the monohalogen compounds enolisation

TABLE II.

*Derivatives of 1:1-dimethylcyclohexane-3:5-dione. M/100-
Solution in 80% ethyl alcohol.*

Time (mins.).	P.		
	4:4-Dichloro-.	4:4-Chlorobromo-.	4:4-Dibromo-.
0	0.1501	0.1953	0.1694
5	0.1968	0.2937	0.2776
10	0.2209	0.3715	0.3434
15	0.2484	0.4272	0.4085
20	0.2646	0.4679	0.4559
30	0.3135	0.5504	0.5362
45	—	0.6521	0.7205
60	0.4271	0.7439	0.9980

is greatly increased, in the dihalogen compounds the reverse obtains and the diketonic structure indicated by the absorption spectra of the compounds is supported.

Similar considerations hold good for the barbituric acids examined:

Acid.	M/100 in water.		M/200 in water.		M/1000 in water.	
	A.	B.	A.	B.	A.	B.
Barbituric	31.463	3.1	50.468	3.5	104.3	3.7
Dibromobarbituric ...	6.710	3.8	9.3305	3.9	20.28	4.0
	M/500 in 50% alcohol.		M/1000 in 25% alcohol.			
		A.		A.		
1-Phenylbarbituric		31.210		80.517		
1-Phenylbromobarbituric ...		34.904		68.117		
1-Phenyldibromobarbituric ...		3.450		9.242		

A = molecular conductivity; *B* = hydrogen-ion concentration.

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