THE DIPOLE MOMENTS AND THE STRUCTURES OF CHLORO- AND BROMO-CROTONOLACTONES

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Abstract—The dipole moments of the isomeric pairs of bromocrotonolactones and of chlorocrotonolactones were measured in benzene solutions at 25° along with those of butyrolactone and crotonolactone. Based on the observed moments of the last two compounds, theoretical calculations were made of the moments of these halocrotonolactones for both α- and β-modifications. The comparison between the observed and calculated moments showed definitely that, of the isomeric pair of bromocrotonolactones, one having a greater moment 4·70 D and a lower melting point 57° is the α-modification and the other isomer having a moment of 3·86 D and a melting point of 77° is the β-modification. Similarly, α-chlorocrotonolactone shows a moment of 4·83 D and melts at 27° while the corresponding β-modification has a moment of 3·57 D and a melting point of 51–52·5°. The result is in good agreement with the conclusion derived from the infra-red absorptions of these compounds and affords an unequivocal evidence in favour of the correctness of the reasoning advanced by Gilman *et al.*, by Whiting, and by Owen and Sultanbawa against the presumption of Hill and his followers. Thus, the long pending problem on the constitutional formulae of isomeric α- and β-halocrotonolactones has been settled.

INTRODUCTION

The problem on the constitutional formulae of isomeric α- and β-halocrotono-lactones has been a subject of considerable dispute. Hill and Cornelison[1] reduced 3:4-dibromocrotonolactone with zinc and acetic acid and obtained bromocrotono-lactone of m.p. 58°. The same compound was obtained, when they treated 3:5-dibromo-2-furoic acid with hydrogen bromide. On the other hand, both the treatment of 3-bromo-2-furoic acid with bromine water and that of 3:5-dibromo-2-furoic acid with bromine gave an isomeric bromocrotonolactone of m.p. 77°. From these methods of synthesis, the former was presumed to be 4-bromocrotonolactone or the β-modifi-cation, while the latter a 3-bromo-compound or the α-modification. Similar synthesis was also carried out for chlorocrotonolactones. Thus, 3:4-dichlorocrotono-lactone and 3:5-dichloro-2-furoic acid gave chlorocrotonolactone of m.p. 25–26°, when they were treated with zinc and acetic acid and with sulphuric acid, respectively. An isomeric chlorocrotonolactone of m.p. 52–53° was obtained, when 3:5- and 4:5-dichloro-2-furoic acids were subjected to reaction with bromine and hydrogen bromide, respectively. The former product was assigned the structure of the β-modification and the latter that of the α-modification. These authors prepared various derivatives of this type and determined their structures on the basis of this
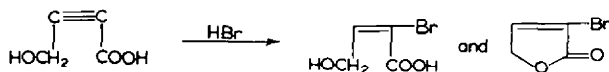
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[1] H. B. Hill and R. W. Cornelison, *Amer. Chem. J.* **16**, 188 (1894).
[2] R. Lespieau and P. L. Viguier, *C.R. Acad. Sci., Paris* **148**, 491 (1909).

conclusion. Later, Lespieau and Viguier[2] prepared a compound identical with the α-modification of Hill and Cornelison by the following reaction.

Thus, a choice was made between the alternatives of the addition of hydrogen bromide on the triple-bonded carbon atoms simply in accordance with the Hill and Cornelison's presumption.

Meanwhile, Gilman et al.[3] pointed out that the structures of substituted 2-furoic acids employed by Hill and his co-worker were in error. Whiting[4] also argued against the simple reasoning of Lespieau and Viguier by calling attention to the general rule that halogen takes the β-position rather than the α-position as they presumed in explaining the reaction that they had carried out. His argument is nothing more or less than the denial of the Hill's original presumption. In the same year, Owen and Sultanbawa[5] prepared bromocrotonolactone of m.p. 59–60° (β-modification according to Hill et al.) from α,β,γ-tribromobutyric acid. Taking account of the fact that the bromine atom at the α-position was the most firmly bound one among the three bromine atoms, they maintained that they obtained ι-bromocrotonolactone. In this prolonged controversy, it was difficult to arrive at ι conclusion, because no arguments carried conviction.

Murakami and Hata[6] have pursued the addition reactions of halogen to methyl 2:5-dimethoxy-2:5-dihydro-2-furoate at its 3:4-positions as well as the ring opening reactions of the resulting addition products. It was found that when dihalo compounds were heated with 50% sulphuric acid they did not suffer a loss of hydrogen halide followed by ring opening as expected, but gave halocrotonolactones (m.p. of bromo- and chloro-compounds, 57° and 27°, respectively) besides some by-products.
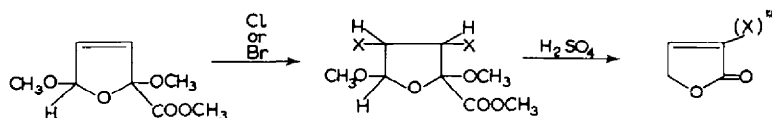
* (X) signifies that the position of X is not yet clear at this stage.

Accordingly, the settlement of the aforementioned question of long standing became an urgent problem. Therefore, for both bromo- and chlorocrotonolactones thus obtained, the isomeric compounds (m.p. of bromo- and chloro-compounds, 77° and 51–52·5° respectively) were prepared by the method of Lespieau and Viguier and their infra-red absorptions were recorded.[6] It was found that the frequency of the C=O band at about 1750 cm^{-1} of the isomer having the lower melting point was higher by 17 cm^{-1} than that of the isomeric partner of the bromo derivatives and the corresponding wave number shift was 25 cm^{-1} for the chloro derivatives. The blue shift of C=O absorptions due to the presence of halogen at the α-position has been amply exemplified with a number of data on substituted aliphatic ketones, cyclohexanones and steroids.[7] Therefore, the isomers having lower melting points were considered to be α-modifications in contradiction to Hill's presumption.

[3] H. Gilman and G. F. Wright, Chem. Rev. 11, 323 (1932); H. Gilman, R. J. Vander Wal, R. A. Franz and E. V. Brown, J. Amer. Chem. Soc. 57, 1146 (1935).
[4] M. C. Whiting, J. Amer. Chem. Soc. 71, 2946 (1949).
[5] L. N. Owen and M. U. S. Sultanbawa, J. Chem. Soc. 3105 (1949).
[6] M. Murakami and Y. Hata, Reported in part at the 11th Annual Meeting of the Chemical Society of Japan, April 1958. To be published.
[7] R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, J. Amer. Chem. Soc. 74, 2828 (1952); E. J. Corey, Ibid. 75, 2301, 3297 (1953); L. J. Bellamy and R. L. Williams, J. Chem. Soc. 4294 (1957)

The present investigation was undertaken in order to confirm this point by dipole moment measurements. This method was hoped to be capable of settling the pending problem by a more direct physical method of attack. For this purpose, measurements were carried out of the moments of four halocrotonolactones mentioned above and some related compounds.

EXPERIMENTAL

Bromocrotonolactone of m.p. 57° and chlorocrotonolactone of m.p. 27° were prepared by Murakami and Hata's[6] method. Bromocrotonolactone of m.p. 77° and chlorocrotonolactone of m.p. 51–52·5° were synthesised by a method due to Lespieau and Viguier.[2] The synthesis of crotonolactone was carried out after Glattfeld et al.,[8] b.p. being 71–72°/7 mm. Commercial butyrolactone was fractionated by means of a Stedman packing column and a fraction boiling at 67·5°/8 mm was taken.

The measurements were carried out at 25° on dilute solutions in benzene. The dielectric constants were measured by means of a heterodyne beat apparatus provided with a platinum cell.[9] For each solute, the determinations of the dielectric constant and density were made on solutions of four different concentrations appropriately chosen below about 0·7 per cent. The graphical plots of the dielectric constant as well as the density of solutions against the concentration in weight per cent gave linear dependence within experimental errors. From the slopes of these straight lines, the molar polarisations of the solutes were calculated by a method similar to that introduced by Halverstadt and Kumler,[10] differing in that densities were used rather than the specific volumes. The sum of electronic and atomic polarisations of each of these compounds was approximated with the molar refraction for the D-line calculated from bond refractions.[11] In order to check the adequacy of this procedure, the refractive indices and densities of butyrolactone and crotonolactone were measured to evaluate $P_E + P_A$. The values were 20·06 and 19·28 cm³, respectively, in good agreement with 20·34 and 20·87 cm³ calculated from bond refractions.

TABLE 1. DIPOLE MOMENTS OF HALOCROTONOLACTONES AND RELATED COMPOUNDS IN BENZENE SOLUTIONS AT 25°. $\varepsilon_1 = 2\cdot2709$, $d_1 = 0\cdot8722$.

Lactones	m.p.	α	β, (g/cm³)	$P_{2\infty}$ (cm³)	MR_D, (cm³)	μ (D)
Butyro-		21·85	0·192	377·0	20·34	4·13
Crotono-		27·48	0·226	457·6	20·87	4·62
Br-crotono-	57°	15·31	0·749	477·2	27·58	4·70
Br-crotono-	77°	10·06	0·519	331·8	27·58	3·86
Cl-crotono-	27°	21·19	0·239	502·2	24·70	4·83
Cl-crotono-	51–52·5°	12·83	0·804	285·3	24·70	3·57

[8] J. W. E. Glattfeld, G. Leavell, G. E. Spieth and D. Hutton, *J. Amer. Chem. Soc.* **53**, 3164 (1931).
[9] Y. Kurita and M. Kubo, *J. Amer. Chem. Soc.* **79**, 5460 (1957); B. Eda, K. Tsuda and M. Kubo, *Ibid* **80**, 2426 (1958).
[10] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.* **64**, 2988 (1942).
[11] A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *J. Chem. Soc.* 514 (1952).

The results are shown in Table 1, in which ε_1 and d_1 denote, respectively, the dielectric constant and density of the solvent; α and β are, respectively, the changes of the dielectric constant and density of the solutions with the weight fraction of the solute; other notations have their usual significances.

DISCUSSION

The only data found in the literature for the moments of these compounds is that of butyrolactone 4·12 D (Marsden and Sutton[12]) in good agreement with 4·13 D of the present investigation.

In order to calculate the theoretical moments for the α- and β-modifications of halocrotonolactones, it is necessary to find the direction of the moment of crotonolactone in the molecule. This was done in the following way. For the sake of simplicity, let it be assumed that five-membered heterocyclic rings take the regular pentagon form. To the first approximation, the moment of butyrolactone may be approximated with the vector sum of the moment of *cyclo*pentanone 2·86 D[13] and that of tetrahydrofuran 1·68–1·71 D.[14] The vector sum of 3·76 D does not perfectly agree with the observed value of 4·13 D. To the second approximation, an additional moment (0·56 D in its magnitude) due to the partial migration of the lone pair electrons of the ring oxygen to the carbonyl oxygen was taken into account in such a way that the resultant moment agrees with the observed value. From these three component moments of known magnitudes and directions, the direction of moment of a butyrolactone molecule could be determined. It points along a direction making an angle of about 19°20' with the C=O direction on the side of the ring oxygen.

A small increase of the moment of crotonolactone over that of butyrolactone can be presumed to have its origin mainly in the partial migration of π-electrons of a C=C double bond in the heterocyclic ring to the carbonyl oxygen. The resulting moment due to this partial migration can be treated by means of the concept of mesomeric moment due to Sutton *et al.*[15] According to their empirical data, the presence of a carbonyl oxygen in this conjugation system induces mesomeric moments of 0·3 D and 0·1 D in the C=C and C—C bonds of C=C—C=O, respectively, with their negative ends pointing to the right. The resultant of the moment of butyrolactone and these mesomeric moments is 4·49 D in fair agreement with the observed value, 4·62 D. It is directed along a line making an angle of 18°50' with the C=O direction on the side of the ring oxygen.

Now that the magnitude and the direction of the moment of crotonolactone have been determined, it is easy to calculate the moments for the α- and β-modifications of halocrotonolactones. The C—Br and C—Cl moments in the molecules of these compounds are approximated with 1·60 D, since the corresponding moments in aromatic molecules are practically the same for bromo and chloro compounds. The theoretical moments thus calculated are shown in Table 2.

The comparison shows definitely that, of the isomeric pair of bromocrotonolactones, one having a greater moment and a lower melting point is the α-modification

[12] R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.* 1383 (1936).
[13] Hs. H. Günthard and T. Gäumann, *Helv. Chim. Acta* **34**, 39 (1951).
[14] L. G. Wesson, *Tables of Electric Dipole Moments*. The Technology Press, Cambridge, Mass. (1948).
[15] J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.* 2957 (1949).

and the other isomer is the β-modification. The same is true for the chlorocrotono-lactones. This affords an unequivocal evidence in favour of the correctness of the reasoning advanced by Gilman *et al.*,[3] by Whiting,[4] and by Owen and Sultanbawa[5] against the presumption of Hill[1] and his followers.[2]

TABLE 2. THEORETICAL MOMENTS OF CROTONOLACTONE AND HALOCROTONOLACTONES COMPARED WITH THE OBSERVED ONES

Lactones	$\mu_{theor.}$	$\mu_{obs.}$
Crotonolactone	4·49 D	4·62 D
α-Bromocrotonolactone	4·74	4·70
β-Bromocrotonolactone	3·01	3·86
α-Chlorocrotonolactone	4·74	4·83
β-Chlorocrotonolactone	3·01	3·57

The agreement between the observed and calculated moments is fairly good for the α-modifications, but is not so good for the β-modifications. This was anticipated, because the lone pair electrons of a halogen atom partly migrate into the conjugated double bond system. The resulting change in moment is smaller for the α-modification, because the geometric configuration leads to the partial cancellation of secondary moments due to conjugation effect, whereas in the β-modification they almost co-operate with one another to give a greater net effect.