

## SHORT COMMUNICATIONS

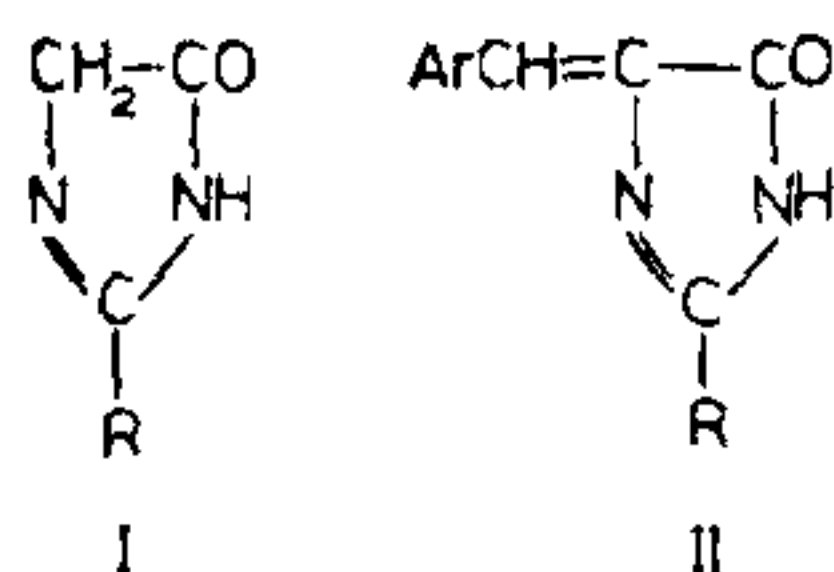
## QUANTITATIVE SYNTHESIS OF 2-ARYL-4-ARYLIDENE-2-IMIDAZOLIN-5-ONES

P. MOHAMED SHAFI

Department of Chemistry, Government College,  
Malappuram 676 509, India.

THE 2,4-disubstituted 2-imidazolin-5-ones have been shown to be a promising material for the synthesis of amino acids and their derivatives<sup>1-4</sup>. The utility of this method lies in the synthesis of 2,4-disubstituted 2-imidazolin-5-ones and their conversion into amino acids and their derivatives in excellent yields. This work gives an improved method by which the first part is accomplished *i.e.* the synthesis of 2-aryl-4-arylidene-2-imidazolin-5-ones (II) in quantitative yields by condensing aromatic aldehydes with a mixture of ethyl iodoacetate and an aromatic amidine hydrochloride in the presence of sodium hydrogencarbonate. The hitherto practical methods<sup>1,5,6</sup> for the synthesis of II gave only fair to excellent yields while the present method gives quantitative yields in all the twelve cases studied.

Devasia and Shafi<sup>3-6</sup> prepared II by condensing aromatic aldehydes with a mixture of ethyl chloroacetate (method A) or ethyl bromoacetate (method B) and an aromatic amidine hydrochloride in the presence of sodium hydrogencarbonate, in 23-71% and 62-97% yields respectively.



The yields of II depend upon the quick formation of I, by the reaction between the haloacetic ester and the aromatic amidine hydrochloride in the presence of sodium hydrogencarbonate, because as soon as I is formed the aromatic aldehyde undergoes Knoevenagel condensation with the active methylene group of I to give II. If the formation of I is delayed the yield of II decreases probably due to the condensation of aromatic aldehyde with amidine to form arylidene derivatives<sup>7</sup>. In method B of Devasia and Shafi<sup>6</sup> the yields of II are considerably better than in method A because in method B I is formed more quickly due to

the higher reactivity of ethyl bromoacetate than ethyl chloroacetate. Therefore it was thought that use of ethyl iodoacetate, which is more reactive than ethyl bromoacetate, would give still better yields of II. Experimentally it was found true and is reflected in table 1.

All the compounds gave satisfactory analytical data for C, H and N.

*Experimental*

Ethyl iodoacetate required for the synthesis was prepared immediately before use by refluxing equimolecular quantities of ethyl chloroacetate and potassium iodide in 2-methylpropan-1-ol for 1 hr.

1. *Amidine hydrochlorides*

Amidine hydrochlorides were prepared by the method of Dox<sup>8</sup>. Benzamidine hydrochloride dihydrate (m.p. 72-73°C), *m*-toluamidine hydrochloride dihydrate (m.p. 52-54°C) and *p*-toluamidine hydrochloride hemihydrate (m.p. 215-17°C) were prepared in 80, 75 and 70% yields respectively.

Table 1 2-Aryl-4-arylidene-2-imidazolin-5-ones(II)

Ar	Yield %	m p <sup>a</sup> (°C)	Lit. m p. (°C)
R = Phenyl			
Phenyl	98	284-85	284-85 <sup>b</sup>
<i>p</i> -Methylphenyl	99	311-12	312-13 <sup>b</sup>
<i>p</i> -Methoxyphenyl	99	302-3	302-3 <sup>b</sup>
3,4-Dimethoxyphenyl	100	268-69	269-70 <sup>b</sup>
R = <i>m</i> -Tolyl			
Phenyl	99	254-56	255-56 <sup>b</sup>
<i>p</i> -Methylphenyl	98	269-70	269-70 <sup>b</sup>
<i>p</i> -Methoxyphenyl	100	237-38	237-38 <sup>b</sup>
3,4-Dimethoxyphenyl	100	246-48	247-48 <sup>b</sup>
R = <i>p</i> -Tolyl			
Phenyl	99	304-5	304-5 <sup>b</sup>
<i>p</i> -Methylphenyl	99	290-92	291-92 <sup>b</sup>
<i>p</i> -Methoxyphenyl	100	269-70	269-70 <sup>b</sup>
3,4-Dimethoxyphenyl	100	262-63	262-63 <sup>a</sup>

<sup>a</sup> crystallised from 2 methylpropan-1-ol.

## 2. 2-Aryl-4-arylidene-2-imidazolin-5-ones

Ethyl chloroacetate (24 mmol) was refluxed with potassium iodide (24 mmol) and 2-methylpropan-1-ol (5 ml) for 1 hr in a round bottomed flask. After cooling to room temperature amidine hydrochloride (15.6 mmol), sodium hydrogencarbonate (50 mmol), aromatic aldehyde (10 mmol) and 2-methylpropan-1-ol (15 ml) were added to it and again refluxed for 1 hr. The product II was filtered and washed with ethanol (3 × 10 ml), water (3 × 10 ml) and again with ethanol (10 ml) and dried in the oven.

The alkali metal iodide may be recovered from the washings and reused.

10 June 1985

1. Kidwai, A. R. and Devasia, G. M., *J. Org. Chem.*, 1962, **27**, 4527.
2. Devasia, G. M. and Pillai, C. R., *Tetrahedron Lett.*, 1975, 4051.
3. Devasia, G. M. and Shafi, P. M., *Indian J. Chem.*, 1980, **B19**, 70.
4. Devasia, G. M. and Shafi, P. M., *Indian J. Chem.*, 1985, (In print).
5. Devasia, G. M. and Shafi, P. M., *Indian J. Chem.*, 1979, **B17**, 526.
6. Devasia, G. M. and Shafi, P. M., *Indian J. Chem.*, 1981, **B20**, 657.
7. Hickinbottom, W. J., *Chemistry of carbon compounds*, (ed.) E. H. Rodd, Elsevier, Amsterdam, Vol IIIA, 1954, p. 564.
8. Dox, A. W., *Organic synthesis*, John Wiley, New York, 1964, p. 5.

## EVALUATION OF SOUND VELOCITY IN MOLTEN HALIDES AT DIFFERENT TEMPERATURES

A. P. SRIVASTAVA

Department of Chemistry, National Degree College, Barhalganj, Gorakhpur 273 402, India.

MANY of the physical properties of ionic liquids are similar in order of magnitude to those of other liquids and due to this molten salts and their multicomponent systems provide an important testing ground for theories of liquids and of solutions.

Various workers have computed sound velocity theoretically in molecular liquids and liquid metals

using cell model theory<sup>1</sup>, hole theory<sup>2</sup>, hard sphere model<sup>3</sup>, significant structure theory<sup>4,5</sup> and Flory's theory<sup>6,7</sup>, but attempts to evaluate sound velocity of molten electrolytes using Flory's statistical theory are rare<sup>8</sup>. The aim of present paper is to extend the Flory theory to evaluate sound velocity of molten halides at different temperatures and to check the validity of the theory in molten halides.

Sound velocity ( $\mu$ ) and the surface tension ( $\sigma$ ) are related by Auerbach<sup>9</sup> relation as

$$\mu = \left( \frac{\sigma}{6.3 \times 10^{-4} \rho} \right)^{2/3}, \quad (1)$$

where  $\rho$  is density.

According to Flory's statistical theory<sup>10,11</sup> the surface tension is expressed as

$$\sigma = \sigma^* \bar{\sigma}(\bar{V}), \quad (2)$$

where  $\sigma^*$  and  $\bar{\sigma}(\bar{V})$  are the characteristic surface tension and reduced surface tension respectively. Patterson and Rastogi<sup>12</sup> in their extension of the corresponding state theory to deal with surface tension used the reduction parameter as

$$\sigma^* = K^{1/3} P^{*2/3} T^{*1/3}. \quad (3)$$

Here  $K$  is the Boltzmann constant.

The characteristic pressure ( $P^*$ ) and characteristic temperature ( $T^*$ ) are given by

$$P^* = \frac{\alpha}{\beta_T} T \cdot \bar{V}^2, \quad (4)$$

$$T^* = \frac{\bar{V}^{4/3} \times T}{(\bar{V}^{1/3} - 1)}, \quad (5)$$

where  $T$ ,  $\alpha$ ,  $\beta_T$  and  $\bar{V}$  are temperature, thermal expansion coefficient, isothermal compressibility and reduced volume respectively. Starting from the work of Prigogine and Saraga<sup>13</sup>, they also derived a reduced surface tension equation of

$$\bar{\sigma}(\bar{V}) = M \bar{V}^{-5/3} - \frac{\bar{V}^{1/3} - 1}{\bar{V}^2} \ln \frac{(\bar{V}^{1/3} - 0.5)}{(\bar{V}^{1/3} - 1)}. \quad (6)$$

In (6)  $M$  is the fractional decrease in the nearest neighbours of a cell due to migration from the bulk phase to the surface phase and has a value from 0.25 to 0.29 on the basis of closed packed lattice. Using (1) in conjunction with (2), (3) and (6) one gets

$$\mu = \left\{ \frac{K P^{*2} \cdot T^*}{6.3 \times 10^{-4} \cdot \rho} \right\}^{2/9} \left[ M \bar{V}^{-5/3} \right]$$