

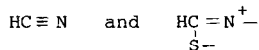
USE OF THIAZOLIUM-2-CARBOXYLATES TO INDUCE BENZOIN CONDENSATIONS

J. Castells\*, F. López Calahorra and L. Domingo.

Departamento de Química Orgánica, Facultad de Química, Universidad de Barcelona  
 Martí i Franquès, 1; 08028 Barcelona. SPAIN

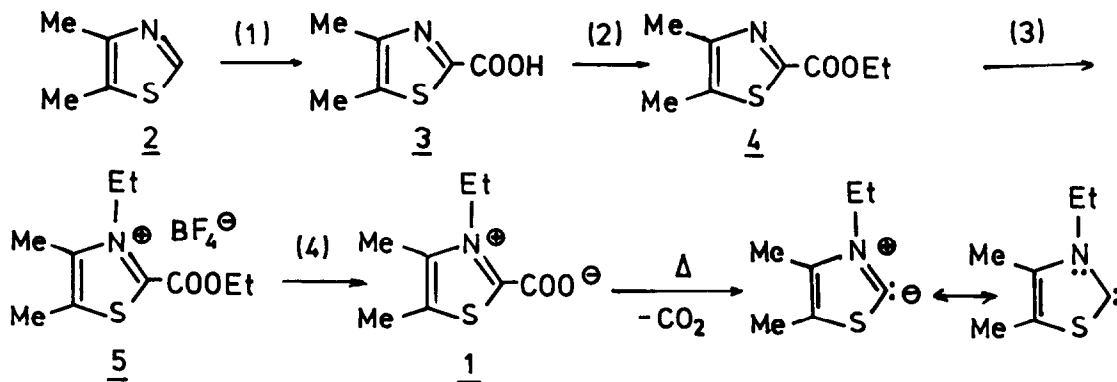
**Abstract.**— The preparation of 3-ethyl-4,5-dimethylthiazolium-2-carboxylate and its use to promote the benzoin condensation and the formoin reaction is described.

It is well known that the benzoin condensation, which is limited to aromatic aldehydes when cyanide is the catalyst, can be extended to aliphatic aldehydes if a thiazolium salt plus base is used instead<sup>1</sup>. The formal electronic analogy between



and some germane experimental evidence on the relatively facile hydrogen isotope exchange at C<sub>2</sub>-H of the thiazolium ring<sup>2</sup> has led to the general acceptance that the actual catalytic species are the corresponding conjugate bases or thiazolin-2-ylidenes. According to this view, generation of thiazolin-2-ylidenes by decarboxylation of the corresponding betaines (a standard preparative procedure used in carbene chemistry<sup>3,4</sup>) should prove an almost ideal way to perform benzoin condensations. With this idea in mind, we have prepared the previously undescribed betaine 1, 3-ethyl-4,5-dimethylthiazolium-2-carboxylate.

Betaine 1 was prepared combining standard procedures (Scheme). Because of its easy



Scheme

1: BuLi;  $\text{CO}_2^5$ ; 2:  $\text{Et}_3\text{O}^+\text{BF}_4^-$ , DIEA,  $\text{CH}_2\text{Cl}_2$ ; 3:  $\text{EtO}_3^+\text{BF}_4^-$ ; 4: Amberlite IRA 401<sup>R</sup> ( $\text{OH}^-$  form)<sup>6</sup>

decarboxylation, it is a rather unstable substance; left to the air at room temperature, observable decomposition of the initially slightly yellow crystals ensues after some minutes. When betaine 1 is added to an ethanol solution of picric acid kept at  $-60^\circ\text{C}$ , 3-ethyl-4,5-dimethylthiazolium picrate<sup>7</sup> crystallizes out.

Betaine **1** is an efficient and clean reagent which allows to conduct benzoin condensations (Table) in the absence of added base and, in this sense, we think it can find ample application. Furthermore, it seems to work even better with aliphatic than with aromatic aldehydes. However, yields are not as spectacularly high as we had expected.

Table . Benzoin condensations

Aldehyde (1.000 g)	Amount of betaine <b>1</b>	Solvent (10 mL)	Temperature	Time	Amount of product <sup>a</sup>
Benzaldehyde	17.4 mg	methanol	reflux	4 h	---
Benzaldehyde	17.4 mg	methanol	reflux	48 h	56 mg
Benzaldehyde	174 mg	methanol	reflux	4 h	595 mg
Benzaldehyde	174 mg	acetonitrile	reflux	4 h	425 mg
Dodecanal	10 mg	methanol	reflux	4 h	362 mg <sup>b</sup>
Dodecanal	10 mg	methanol	reflux	48 h	261 mg <sup>b</sup>
Dodecanal	100 mg	methanol	reflux	4 h	712 mg
Dodecanal	100 mg	acetonitrile	reflux	4 h	607 mg

a. Yields are in recrystallized product: benzoin, m. p. 133-4°C; dodecain. m. p. 63-64°C.

b. Recrystallization was unsatisfactory and some dodecain was lost as an oily residue.

Betaine **1** is also a very convenient reagent for the formoin reaction<sup>8</sup> (Figure).

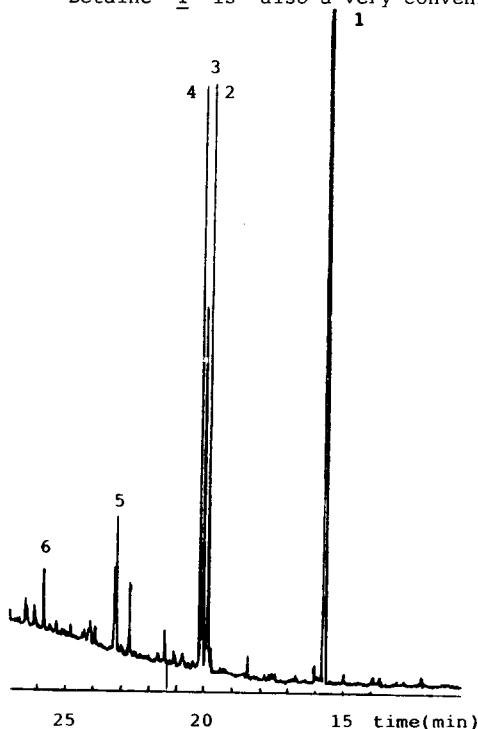


Figure.- TMS-oximes<sup>9</sup> of formoin aliquots directly derivatized. A 25 m crosslinked 5% phenylmethylsilicone capillary column was used; temperature programme:  $T_1 = 80^\circ$ ,  $t_1 = 2$  min, rate =  $6^\circ/\text{min}$ . 1, dihydroxyacetone; 2, 4, erythrose; 3, 2-hydroxy-methylglyceraldehyde; 5, C<sub>5</sub>-sugars; 6, C<sub>6</sub>-sugars.

### Experimental

**Benzoin condensations.**- After refluxing for the reported time (Table), the cold reaction mixture was poured into water (75 mL) and the precipitate was filtered off and recrystallized from ethanol. Several experiments using slightly modified procedures (changing the order of addition of reactants, operating in absence of solvent, etc.) did not afford substantial differences.

**Formoin reaction.**- A mixture of paraformaldehyde (976 mg), betaine **1** (200 mg) and anhydrous acetonitrile (10 mL) was heated at  $60^\circ\text{C}$  for 24 h. After 5 min all the paraformaldehyde had dissolved. Samples were withdrawn and gas-chromatographically analyzed after 20 min, 2, 6 and 24 h. The four chromatograms were practically identical. Figure gives the one registered after 24 h.

### References and notes.

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