

## Ethanolysis of 2-Substituted-4-arylidene-5-oxazolones. Effect of Trifluoromethyl Substitution on the Arylidene Ring

ROBERT FILLER AND HERMAN NOVAR

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The ultraviolet absorption spectra of azlactones are usually measured in 95% ethanol, chloroform, ether, or acetic acid as solvents. A hypsochromic shift of the principal maximum of unsaturated azlactones has been observed<sup>1</sup> when dilute ethanolic solutions were allowed to stand at room temperature for several days. This shift is due to the noncatalyzed solvolysis of the oxazolone to form the open chain ester and this change offers a convenient means for following the course of the reaction spectrophotometrically.

Thus, 2-phenyl-4-benzylidene-5-oxazolone (Ia),  $\lambda_{\max}^{\text{EtOH}}$  360  $m\mu$ <sup>2</sup> was gradually converted into ethyl  $\alpha$ -benzamido cinnamate (IIa),  $\lambda_{\max}^{\text{EtOH}}$  282  $m\mu$ . After three to four days, about 50% conversion had occurred and the reaction was complete within twenty-one days.<sup>1</sup> We have confirmed these results and have further observed that 2-methyl-4-benzylidene-5-oxazolone (Ib),  $\lambda_{\max}$  328  $m\mu$ , was much more readily solvolyzed to IIb,  $\lambda_{\max}$  281  $m\mu$ , with conversion almost complete after twenty-eight hours. This increased rate of alcoholysis of 2-methyl analogs has been observed previously with another oxazolone<sup>1</sup> and is consistent with the facile hydrolysis of Ib with boiling water-acetone to give the  $\alpha$ -acetamido acid.<sup>3</sup> Ia is stable under the latter conditions.

In the course of our studies on trifluoromethyl-substituted aromatic amino acids, we have prepared and similarly examined several analogs of Ia and Ib (see Table I), possessing trifluoromethyl groups in the *ortho* and *meta* positions of the arylidene ring. The preparation of these compounds will be discussed in a forthcoming paper.<sup>4</sup>

Ic ( $\lambda_{\max}$  359  $m\mu$ ) was largely converted to the open-chain,  $\alpha,\beta$ -unsaturated ester after twenty-four hours and had reacted completely within seventy-two hours, while the *meta* trifluoromethyl compound, Id ( $\lambda_{\max}$  358  $m\mu$ ), and the 2-methyl counterparts, Ie ( $\lambda_{\max}$  324  $m\mu$ ) and If ( $\lambda_{\max}$  322  $m\mu$ ), showed no evidence of unchanged oxazolone after twenty four hours.

These results reflect the enhancement of solvolysis due to the electronic influence of the trifluoromethyl group in labilizing the oxazolone ring. The

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TABLE I

$$\begin{array}{c} \text{RCH}=\text{C}-\text{C}=\text{O} \\ | \quad | \\ \text{N} \quad \text{O} \\ \diagdown \quad / \\ \text{C} \\ | \\ \text{R}' \end{array} + \text{C}_2\text{H}_5\text{OH} \longrightarrow \begin{array}{c} \text{RCH}=\text{C}-\text{COOC}_2\text{H}_5 \\ | \\ \text{NHCOR}' \end{array}$$

I II

Compound	Substituents	
	R	R'
a	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>
b	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>
c	<i>o</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>
d	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>
e	<i>o</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	CH <sub>3</sub>
f	<i>m</i> -C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	CH <sub>3</sub>

site of attack is the lactone carbonyl moiety and it is difficult, as the results are not quantitative, to evaluate, particularly in the case of the *o*-trifluoromethyl compound, the relative importance of the *inductive* and *field* effects in the total electrical effect. Such an evaluation has been made by Roberts<sup>5</sup> for *o*-substituted phenylpropionic acids and esters.

It is also of interest to note that the spectra of the 2-phenyl-4-trifluoromethylbenzylidene-5-oxazolones (Ic and Id) did not reveal any sign of *trans*-acylation during their preparation by the Erlenmeyer-Plöchl reaction, in contrast to the observations of Bennett and Niemann in the preparation of the 4-(*p*-fluorobenzylidene) analog.<sup>6</sup>

Concentrations of solutions were about 5  $\mu\text{g}$  oxazolone/cc. Measurements were made with a Beckman DK-2 spectrophotometer.

DEPARTMENT OF CHEMISTRY  
ILLINOIS INSTITUTE OF TECHNOLOGY  
CHICAGO 16, ILL.

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(6) E. L. Bennett and C. Niemann, *J. Am. Chem. Soc.*, **72**, 1803 (1950).

## The Synthesis of a Novel Ester of Phosphorus and of Arsenic

J. G. VERKADE<sup>1a</sup> AND L. T. REYNOLDS<sup>1b</sup>

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Stetter and Steinacker<sup>2</sup> report the synthesis of 1-phospha-2,8,9-trioxa-adamantane (II) and the corresponding 1-oxide and 1-sulfide. Using a modification of their synthetic method, we have pre-

(1a) Present address: Department of Chemistry, University of Illinois, Urbana, Illinois.

(1b) Present address: Department of Chemistry, Cornell University, Ithaca, New York.

(2) H. Stetter and K. Steinacker, *Ber.*, **85**, 451 (1952).