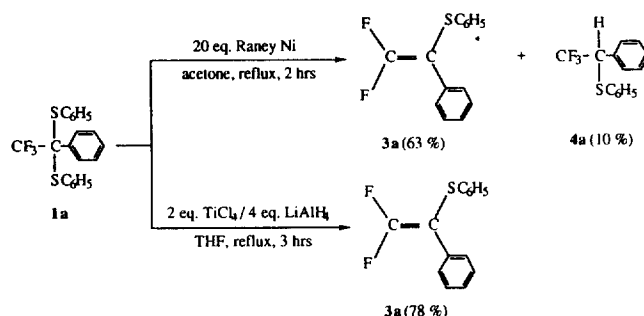


Table 1. Preparation of 1H, 1H-perfluoroalkyl Aromatic Compounds 2
$$\begin{array}{c} \text{SC}_6\text{H}_5 \\ | \\ \text{R}_F-\text{C}-\text{R} \\ | \\ \text{SC}_6\text{H}_5 \\ \mathbf{1} \end{array} \xrightarrow[80-90^\circ\text{C}, 1 \text{ hr, no solvent}]{2.2 \text{ eq. Bu}_3\text{SnH}/10 \text{ mol\% AIBN}} \begin{array}{c} \text{H} \\ | \\ \text{R}_F-\text{C}-\text{R} \\ | \\ \text{H} \\ \mathbf{2} \end{array}$$

| Compound No. | R | R _F | 2, yield (%) ^a |
|--------------|---|---|---------------------------|
| 1a | | CF ₃ | 80 |
| 1b | | CF ₃ | 84 |
| 1c | | CF ₃ | 82 |
| 1d | | CF ₃ | 83 |
| 1e | | CF ₃ | 84 |
| 1f | | CF ₃ | 73 |
| 1g | | CF ₃ | 92 |
| 1h | | CF ₃ | 85 |
| 1i | | CF ₃ | 87 |
| 1j | | CF ₃ | 78 |
| 1k | | CF ₃ CF ₂ | 96 |
| 1l | | CF ₃ CF ₂ CF ₂ | 90 |

^aIsolated yields.

in THF at reflux temperature for 3 hours afforded only **3a** in 78% yield. In this reaction products **2a** and **4a** were not detected.



Acknowledgment. The authors thank the Ministry of Science and Technology and the Yonsei University for financial support, and professor S. K. Choi (KAIST) for recording the ¹⁹F NMR spectra.

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A Facile Synthesis of 5(4H)-Oxazolones

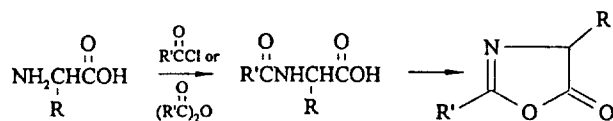
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Received March 7, 1994

5(4H)-Oxazolones which are considered anhydrides of *N*-acyl- α -amino acids have been employed as intermediates¹ for various organic synthesis, especially in the field of α -amino acid, peptide and penicillin chemistry. Recently, Saegusa² reported a new ring opening polymerization of 5(4H)-oxazolone and its derivatives to synthesize various poly (*N*-formyl- α -peptides) in order to develop stimuli sensitive polymers and reemphasized their application as valuable monomers in polymer chemistry.

Unsaturated 5(4H)-oxazolones were synthesized by the condensation of benzaldehyde with hippuric acid in the presence of an acetic anhydride by Plöchl³ in 1883. Mohr and coworkers³ prepared several saturated 5(4H)-oxazolones by the reaction using an acetic anhydride and *N*-acyl- α -amino acids. In general, 5(4H)-oxazolones have been prepared by cyclization of *N*-acyl- α -amino acids treated with an excess acetic



- 1 R=H R'=Me
 2 R=H R'=Ph
 3 R=Me R'=Ph
 4 R=Ph R'=Ph

Scheme 1.

Table 1. The Synthesis of 5(4H)-oxazolones

| R R' | Reagent | Solvent | Temp(°C) | Yield (%) |
|-------|--|--|----------|-----------|
| 1 | EtO ₂ CCl/Et ₃ N | Benzene | RT | 53.0 |
| | DCC | CH ₂ Cl ₂ /PhNO ₂ | RT | 42.3 |
| H Me | Ac ₂ O | Ac ₂ O | 70 | . |
| 2 | EtO ₂ CCl/Et ₃ N | Benzene | 40 | 77.5 |
| | DCC | CH ₂ Cl ₂ | RT | . |
| H Ph | Ac ₂ O | Ac ₂ O | 70 | 48.3 |
| 3 | EtO ₂ CCl/Et ₃ N | Benzene | 60 | 77.3 |
| | DCC | CH ₂ Cl ₂ | RT | . |
| Me Ph | Ac ₂ O | Ac ₂ O | 70 | 53.6 |
| 4 | EtO ₂ CCl/Et ₃ N | Benzene | RT | 73.4 |
| | DCC | CH ₂ Cl ₂ | RT | . |
| Ph Ph | Ac ₂ O | Ac ₂ O | 70 | 46.5 |

anhydride or an equimolar amount of *N,N'*-dicyclohexylcarbodiimide (DCC).² When an acetic anhydride was employed as a dehydrating reagent, an acetic acid generated during the reaction caused difficulties to isolate an acid and/or thermally sensitive products.⁴ In case of DCC, a removal of an unreacted DCC from the reaction mixture was cumbersome to obtain the desired products in pure form. For example, 2-methyl-5(4H)-oxazolone **1**⁵ prepared under the above reaction conditions has not been fully characterized since it was decomposed during the above workup processes. In spite of a wide application of 5(4H)-oxazolones,⁶ reliable synthetic methods of 5(4H)-oxazolones have not been reported in the literature.

During investigation for a ring opening polymerization of 5(4H)-oxazolones, a facile synthetic route for 5(4H)-oxazolones utilizing an ethyl chloroformate was developed (Scheme 1).

N-acyl- α -amino acids were reacted with an equimolar amount of ethyl chloroformate and triethyl amine in benzene at room temperature to provide the desired 5(4H)-oxazolones in consistent and good yield. A vigorous evolution of CO₂ gas was observed during the reaction. Since a removal of CO₂ gas was irreversible, a conversion of *N*-acyl- α -amino acids to 5(4H)-oxazolone put forward to be completed. In addition, an isolation of the products was simplified by filtration of a triethylamine hydrochloride salt. When a mole ratio of starting material was changed, the reaction was proceeded faster but provided the lower yield.

Our results are summarized in Table 1.⁷ The known procedures⁸ were not able to afford these compounds in consistent yield since reaction conditions were too harsh to isolate the sensitive products. Under the our reaction condition, thermally sensitive **1**⁹ was prepared in pure form and fully characterized for the first time in the literature. 2-Phenyl-5(4H)-oxazolone **2** was obtained in the 77.5% yield compared to 48.5% yield by using an acetic anhydride.

In conclusion, a mild and efficient synthetic route for various 5(4H)-oxazolones is developed. Scope and limitation of our procedure are currently under investigation.

Acknowledgement. We thank the Korea Science Foundation for generous support (92-23-00-02) for this research. We also thank Organic Research Center for GC-MS and Elementary Analysis data.

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