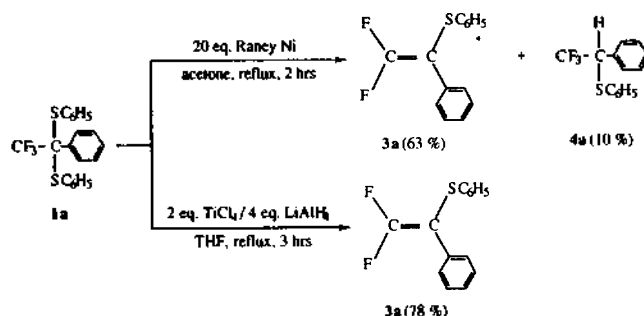


Table 1. Preparation of 1H, 1H-perfluoroalkyl Aromatic Compounds 2

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.



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A Facile Synthesis of 5(4H)-Oxazolones

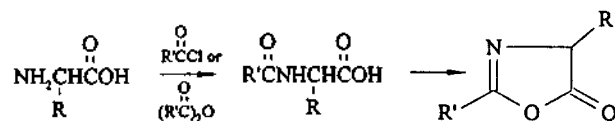
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5(4H)-Oxazolones which are considered anhydrides of *N*-acyl- α -amino acids have been employed as intermediates¹ for various organic synthesis, especially in the field of α -amino acid, peptide and penicillin chemistry. Recently, Saegusa² reported 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,⁵ 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.

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