

Reaction of γ -Picoline *N*-Oxide with Ketenimines in the Presence of Organic Acids: Preparation of α -Acyloxyamides

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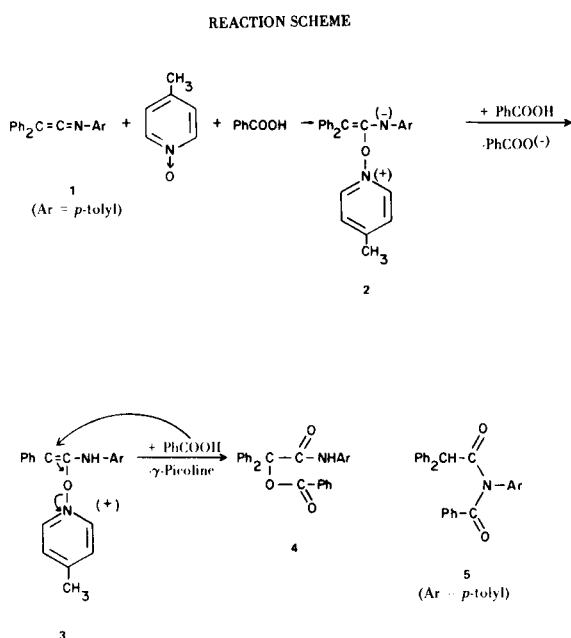
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A synthesis of α -acyloxyamides is described which utilizes the reaction of γ -picoline *N*-oxide and various organic acids with diphenylketene *N*-*p*-tolylimine.

J. Heterocyclic Chem., 13, 1351 (1976).

Sir:

We have observed that when diphenylketene *N*-*p*-tolylimine (**1**) is treated with excess γ -picoline *N*-oxide and benzoic acid, an 86% yield of *N*-(*p*-tolyl)- α -benzoxydiphenylacetamide (**4**) is obtained (1). No other product was isolated from the reaction mixture. Earlier, Stevens observed that treatment of **1** with benzoic acid yielded the imide **5** (2). Thus, the presence of γ -picoline *N*-oxide totally changes the mode of reaction of ketenimines with benzoic acid.



One reasonable explanation of these results is illustrated by the REACTION SCHEME. The reaction is initiated by a nucleophilic attack of the oxide on the ketenimine to give **2**, a strong nucleophile which would be readily

protonated to yield **3**. Since **3** should be receptive to a nucleophilic attack by the organic acid with the subsequent elimination of γ -picoline and loss of a proton, this intermediate would allow for the formation of the product observed (**4**).

To test the generality of this reaction as a route to α -acyloxyamides, **1** was treated with γ -picoline *N*-oxide in the presence of acetic acid, propionic acid, cyclohexanecarboxylic acid, and diphenylacetic acid. The corresponding α -acyloxyamides were obtained in 56% (**3**), 78%, 77% and 70% yields, respectively (**5**). Although the imide analogous to **5** was obtained in the reaction with acetic acid in 32% yield, the imide adduct was not observed in reactions with the other carboxylic acids.

The reaction of ketenimines with γ -picoline *N*-oxide and organic acids appears to be a general route to α -acyloxyamides. The ease of carrying out the reaction, the variety of ketenimines that are readily synthesized (**6**), the commercial availability of the *N*-oxides and the acids, and the good yields obtained indicate this process should be a synthetically significant route to α -acyloxyamides.

REFERENCES AND NOTES

- (1) A typical run is as follows: a solution of 0.01 mole of **1**, 0.06 mole of γ -picoline *N*-oxide, and 0.06 mole of benzoic acid in 100 ml. of chloroform is heated to reflux for one hour. The solution is then washed free of acid with aqueous sodium bicarbonate, dried over anhydrous sodium sulfate, and concentrated to 20 ml. The addition of 40 ml. of petroleum ether results in the precipitation of **4**. Recrystallization of this material from ethanol gives analytically pure **4** in 86% yield, m.p. 167-169° (lit. (4) 163-164°). The sample exhibited strong ir absorptions at 1705, 1600, 1500, and 1275 cm^{-1} , and the ms exhibited the parent ion at m/e 421 (3%). Other m/e values and relative abundances are 300(21%), 299(100%) and 212(100%) for loss of PhCOO , and 165(80%) for $\text{Ph}_2\text{C}^\dagger$.

(2) C. L. Stevens and M. E. Munk, *J. Am. Chem. Soc.*, **80**, 4065 (1958).

(3) Proof of structure for *N*-(*p*-tolyl)- α -acetoxydiphenylacetamide is based on the ir, nmr, and ms of the sample and on m.p. comparison with the literature value (4).

(4) H. Kagen and I. Lillien, *J. Org. Chem.*, **31**, 3728 (1966).

(5) Proof of structure for each of the previously unreported α -acyloxyamides is as follows: A. *N*-(*p*-Tolyl)- α -propionoxydiphenylacetamide: m.p. 181-182°; ir: (1720, 1700, 1600, and 1515 cm^{-1}); nmr: [1.2 δ (t, 3H), 2.32 δ (s, 3H), 2.6 δ (q, 2H), 6.9-8.3 δ (m, 15H)]. *Anal.* Calcd. for $\text{C}_{24}\text{H}_{23}\text{NO}_3$: C, 77.18, H, 6.20; N, 3.75. Found: C, 77.39; H, 6.30; N, 3.77. B. *N*-(*p*-Tolyl)- α -cyclohexylcarboxydiphenylacetamide: m.p. 132-133°; ir: (1725, 1700, 1600, 1515 cm^{-1}); nmr: [0.4-2.8 δ (m, 11H), 2.3 δ (s, 3H), 6.7-8.2 δ (m, 15H)]. *Anal.* Calcd. for

$\text{C}_{28}\text{H}_{29}\text{NO}_3$: C, 78.66; H, 6.83; N, 3.27. Found: C, 78.39; H, 6.94; N, 3.44. C. *N*-(*p*-Tolyl)- α -diphenylacetoxydiphenylacetamide: m.p. 121-123°; ir: (1730, 1700, 1600, and 1515 cm^{-1}); nmr: [2.31 δ (s, 3H), 6.31 (s, 1H), 7.15-8.0 (m, 25H)]. *Anal.* Calcd. for $\text{C}_{35}\text{H}_{29}\text{NO}_3$: C, 82.16; H, 5.71; N, 2.74. Found: C, 81.99; H, 5.96; N, 3.00.

Analyses were performed by the Heterocyclic Chemical Corporation of Harrisonville, Missouri; ir were determined on a Perkin-Elmer Infracord in potassium bromide wafers or neat; nmr were determined on a Jeolco Minimar in deuteriochloroform; and the mass spectra were determined with a DuPont Model 490 mass spectrometer.

(6) H. Bestmann, J. Lienert, and L. Mott, *Ann. Chem.*, **718**, 24 (1968) and C. L. Stevens and G. H. Singhal, *J. Org. Chem.*, **29**, 34 (1964).