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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

A New Method for the Synthesis of Furan Derivatives

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Published online: 24 Sep 2006.

To cite this article: M. Venugopal , B. Balasundaram & P. T. Perumal (1993) A New Method for the Synthesis of Furan Derivatives, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 23:18, 2593-2597

To link to this article: http://dx.doi.org/10.1080/00397919308012593

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SYNTHETIC COMMUNICATIONS, 23(18), 2593-2597 (1993)

A NEW METHOD FOR THE SYNTHESIS OF FURAN DERIVATIVES

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Abstract : Substituted 2-chloro-4-formyl-5-arylfuran and 2,5-dimethyl-3-formylfuran derivatives were synthesised from their corresponding substituted 3-benzoylpropionic acid and acetonylacetone using Vilsmeier reagent in good yields.

Furan derivatives form key intermediates for natural product synthesis and also derivatives[1-5] for a wide range of biologically active compounds. Efficient synthesis of furans continue to be of interest in view of the widespread occurrence of this system in Nature[6]. Vilsmeier-Haack reaction is a mild method for formylation[7], acylhalo addition[8] and ring annulation[9]. Vilsmeier reaction on acids have not been widely studied[10]. In continuation of our studies on carbonyl compounds[11] with Vilsmeier reagent, we became interested in the study of some substituted 1,4-dicarbonyl moiety namely 3-benzoylpropionic acids and acetonylacetone. Acidic reagents bring about the cyclization of 1,4-diketone and 3-benzoylpropionic acid to give furan[12] and naphthoquinone respectively, but in Vilsmeier reaction condition 1,4-diketone and 3-benzoylpropionic acids gave

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formylated furan and chloroformylfurans respectively. 3-Benzoylpropionic acids on reaction with Vilsmeier reagent ($DMF/POCl_3$) at 80-90°C gave 2-chloro-4-formyl-5-arylfurans (2) in good yields. Similarly 2,5-dimethyl-3- formyl furan (4) has been prepared by subjecting acetonylacetone (3) with Vilsmeier reagent at 80-90°C. The products are listed in Table 1.

When the above reactions were carried out below 80°C no reaction has taken place, only starting compound was recovered, and above 100°C only viscous uncharacterisable material was obtained. Our method will be the first one to report such a kind of cyclization reaction on keto acids using Vilsmeier reagent. Various keto acids have been prepared by Fridel-Crafts acylation of substituted benzenes with succinic anhydride[13] (scheme 1).

Scheme:1

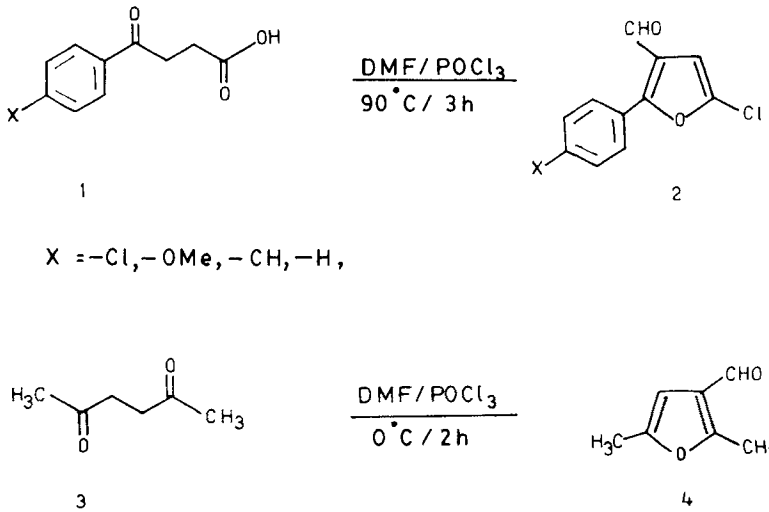

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Table 1. Reaction products of 1,4-ketoacids and acetonylacetone with DMF and $POCl_3$

S.No	Substrate	Product[a]	m.p'c	Yield %
1.	3-benzoyl propionic acid (1a)	2-chloro-4-formyl-5-phenyl furan (2a)	98	75
2.	3-(4-methyl benzoyl) Propionic acid (1b)	2-chloro-4-formyl-5-(4-methylphenyl) furan (2b)	122	70
3.	3-(4-methoxy benzoyl) propionic acid (1c)	2-chloro-4-formyl -5-(4-methoxy phenyl)furan (2c)	101	85
4.	3-(4-chloro benzoyl) propionic acid (1d)	2-Chloro-4-formyl -5-(4-chloro phenylfuran (2d)	140	80
5.	Acetonylacetone (2)	2,5-dimethyl-3-formylfuran (4)	80	60

a. All products gave satisfactory C,H analysis.

The spectral data of the new compounds agreed well with the assigned structures. The IR spectra of the furan showed absorption at 1661 cm^{-1} attributable to C=O group of the aldehyde. The ^1H NMR spectra showed the olefinic (HC=C-) proton at δ6.93, and the aldehyde proton showed a signal at δ9.87.

TYPICAL PROCEDURE :
Preparation of 2-chloro-4-formyl-5-phenylfuran:

3-Benzoylpropionic acid (10 mmol) was dissolved in 6 ml of DMF and was cooled to 0°C and 4 ml of $POCl_3$ was added dropwise over 40 minutes and stirred for 1h at room

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temperature and for 4h at 80°C. The reaction mixture was then poured with stirring onto a mixture of crushed ice (100g) containing sodium acetate (5g) and water (30ml). The product was extracted with chloroform (3x50 ml) and dried over anhydrous sodium sulfate. After removal of the solvent, the crude product was chromatographed through a short column of silica gel using 1:9 ratio of chloroform and petroleum ether as eluent to provide 2-chloro-4-formyl-5-phenylfuran. IR(KBr): 1168, 1652, 1661 cm^{-1}; ^1H NMR ($CDCl_3$); δ 6.93 (s,1H,=CH-), 7.32-7.6 (m,5H,Ar-H) 9.87 (s,1H, -CHO); ^{13}C NMR ($CDCl_3$); δ 103.15, 123.95, 128.57, 128.69, 128.84, 144.75, 154.91, 183.1; Ms (m/e): 206 (M^+).

Acknowledgement: The authors are thankful to CSIR and UGC New Delhi for financial support.

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(Received in The Netherlands 14 April 1993)

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