Tetrahedron Letters, Vol.22, No.34, pp 3269 - 3272, 1981
Printed in Great Britain

0040-4039/81/343269-04$02.00/0

FACILE SYNTHESIS OF 4-SUBSTITUTED BUTENOLIDES FROM FURAN[1]

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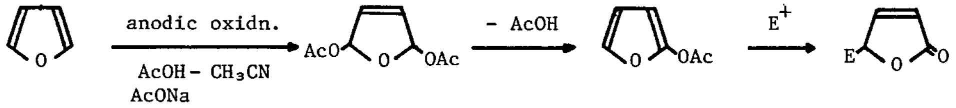
A variety of 4-substituted butenolides were prepared utilizing 2-acetoxyfuran as a key intermediate which can be easily synthesized by anodic oxidation of furan.

Although 2-mono-[2] or 2,5-bis(trimethylsiloxy)furans[3] have recently been shown to be useful for the synthesis of 4-substituted butenolides and bisbutyrolactones, their use as starting materials is highly limited because of their instability. We report herein a new synthetic method of 4-substituted butenolides (**3**) utilizing 2-acetoxyfuran (**2**), which is sufficiently stable to allow the reaction of **2** with several kinds of electrophiles (E^+) under various conditions (eq. 1). Further advantage of our method is the facile preparation of **2**, which can be synthesized by using the method of anodic oxidation (eq. 1).

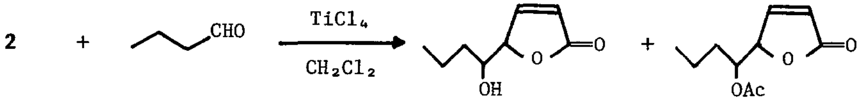


1 **2** **3** (1)

Anodic oxidation of furan in acetic acid or in a mixture of acetic acid and acetonitrile containing sodium acetate gave 2,5-dihydro-2,5-diacetoxyfuran (**1**). The yield hitherto reported to be very low[4] was improved by carrying out the reaction as described below.

Into a cell equipped with platinum anode and carbon rod cathod was added a solution of furan (2.0 g) in a mixture of acetic acid (40 ml) and acetonitrile (10 ml) containing sodium acetate (2.0 g), and the mixture was cooled to 3~7 °C with ice-water bath during the reaction. After 2.45 *F*/mol of electricity was passed, the reaction mixture was poured into water and extracted with CH_2Cl_2. The extracts were dried with $MgSO_4$ and distilled to give **1** in a 57% yield.[5] The conversion of **1** to **2** was accomplished in a 61 - 81% yield by the method of Cava.[8]

Reaction of **2** with electrophiles was carried out by the following way. To a stirred solution of butyraldehyde (5.2 mmol) and $TiCl_4$ (4.0 mmol) in CH_2Cl_2 (8 ml) was added a solution of **2** (4.0 mmol) in CH_2Cl_2 (2 ml) at - 78 °C. After the addition was completed, the reaction mixture was allowed to stand at - 78 °C for additional 2 h, warmed to room temperature, and poured into water successively. The aqueous solution was saturated with sodium chloride and extracted with CH_2Cl_2 (3 X 20 ml). The organic layer was dried with $MgSO_4$ and treated with column chromatograph to yield two products, **4a** and **4b** (eq. 2).

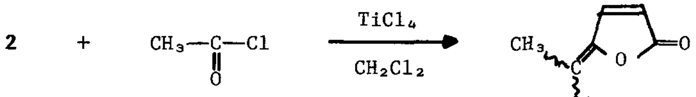


4a **4b**

(2)

Lewis acids other than $TiCl_4$ were also effective for this reaction,[9] though the ratio of **4a** and **4b** depended on the nature of Lewis acids. Results are shown in Table I[10] which also indicates the results of the reaction of **2** with methylal and methyl orthoformate.

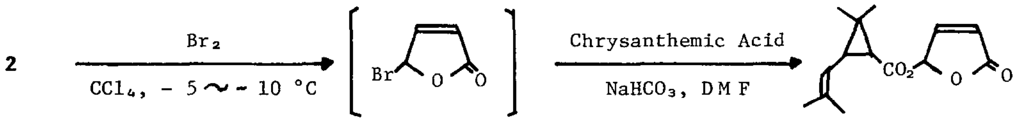
The Friedel-Crafts type reaction of **2** was also achievable as described below (eq. 3). Thus, to a stirred solution of acetyl chloride (6.0 mmol) and $SnCl_4$ (6.0 mmol) in CH_2Cl_2 (4 ml) was added slowly a solution of **2** (2.0 mmol) in CH_2Cl_2 (6 ml) at - 78 °C (1 h). After addition was completed, the reaction mixture was stirred at - 78 °C for 3.5 h and allowed to stand at room temperature overnight. The usual working up gave **8** in a 50% yield.[10,13]



8

(3)

Furthermore, the high potentiality of **2** in organic synthesis is shown in the synthesis of an analogue (**10**) of pyrethroids which is a powerful insecticide (eq. 4).[10,13]

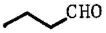
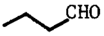
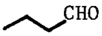
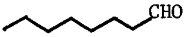
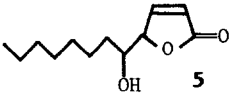
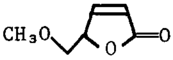
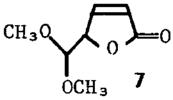


9 **10**

(4)

After addition of bromine (4.0 mmol) to **2** (4.0 mmol) in CCl_4 at - 5 ~ - 10 °C, evaporation of the solvent *in vacuo* gave a crude product of **9**,[11] which was added into a solution of chrysanthemic acid (8.0 mmol) in dry DMF (8 ml) containing $NaHCO_3$[12] (16.0 mmol). The solution was allowed to stand overnight at room temperature and the usual working up gave **10** in a 48% yield.

Table I.   Reaction of **2** with Electrophiles.

Electrophiles (mmol)		Lewis Acid (mmol)	Products (Yield, %)[c]
	(5.2)	$TiCl_4$ (4.0)[a]	**4a** (70) **4b** (8)
	(5.2)	$TiCl_4$ (2.0)[a]	**4a** (67) **4b** (6)
	(5.2)	$SnCl_4$ (4.0)[a]	**4a** (18) **4b** (52)
	(5.2)	$BF_3{\cdot}OEt_2$ (4.0)[a]	**4a** (21) **4b** (55)
	(5.2)	$TiCl_4$ (4.0)[a]	 (60) **5**
$CH_2(OCH_3)_2$	(8.0)	$TiCl_4$ (4.0)[a]	 (86) **6**
$CH(OCH_3)_3$	(2.6)	$TiCl_4$ (2.0)[b]	 (89) **7**

a) The amount of **2** was 4.0 mmol.

b) The amount of **2** was 2.0 mmol.

c) ^{1}H-NMR: **4a**; δ (CCl_4) 0.93 (3H, br t), 0.95-1.87 (4H, m), 3.54 (1H, br), 3.73 (1H, m), 4.84 (1H, m), 6.02 (1H, dd), 7.44 (1H, dd).

4b; δ (CCl_4) 0.91 (3H, br t), 1.10-1.95 (4H, m), 2.00 and 2.04 (3H, s 4.90-5.28 (2H, m), 6.08 (1H, dd), 7.47 (1H, dd).

5 ; δ (CCl_4) 0.92 (3H, br t), 1.10-1.88 (12H, m), 3.20-3.69 (2H, m), 4.99 (1H, m), 6.09 (1H, dd), 7.66 (1H, dd).

6 ; δ (CCl_4) 3.36 (3H, s), 3.56 (2H, d), 5.04 (1H, m), 6.03 (1H, dd), 7.46 (1H, dd).

^{1}H-NMR spectra of **7** was identified with reported value.[2b]

References and Notes

1) Electroorganic Chemistry. 54.

2) a) E. Yoshii, T. Koizumi, E. Kitatsuji, T. Kawazoe, and T. Kaneko, *Heterocycles*, **4**, 1663 (1976).

b) M. Asaoka, N. Sugimura, and H. Takei, *Bull. Chem. Soc. Jpn.*, **52**, 1953 (1979).

3) P. Brownbridge and T. Chan, *Tetrahedron Lett.*, **21**, 3427 (1980). *Idem.*, *ibid.*, **21**, 3431 (1980).

4) The reported yield was only 12%. A. J. Baggaley and R. Brettle, *J. Chem. Soc. (C)*, **1968**, 969.

5) The preparation of **1** from furan is also attainable by the method using $Pb(OAc)_4$[6] or Br_2.[7]

6) N. Eleming and N. Clauson-Kaas, *Acta Chem. Scand.*, **6**, 535 (1952).

7) N. Clauson-Kaas, A. Lie, and N. Eleming, *Acta Chem. Scand.*, **4**, 1233 (1950).

8) M. P. Cava, C. L. Wilson, and C. J. Williams, Jr., *J. Am. Chem. Soc.*, **78**, 2303 (1956).

9) In the case of 2-(trimethylsiloxy)furan, Lewis acid other than tin tetrachloride gave poor results.[2]

10) All the products were identified by the spectroscopic and elemental analyses.

11) N. Eleming, *et al.* reported the synthesis of **9**; N. Eleming and N. Clauson-Kaas, *Acta Chem. Scand.*, **6**, 565 (1952).

12) The esterification was carried out according to a general method reported by R. Marchelli *et al.*

V. Bocchi, G. Casnati, A. Dossena, and R. Marchelli, *Synthesis*, **1979**, 961.

13) ^{1}H-NMR: **8**; one isomer δ ($CDCl_3$) 2.10 (3H, s), 2.21 (3H, s), 6.05 (1H, d), 7.50 (1H, d), the other isomer δ ($CDCl_3$) 2.23 (6H, s), 6.05 (1H, d), 7.47 (1H, d).

10; δ (CCl_4) 0.71-2.03 (2H, m), 1.13 (3H, s), 1.30 (3H, s), 1.73 (6H, br s), 5.88 (1H, m), 6.23 (1H, dd), 6.94 (1H, m), 7.39 (1H, dd).

(Received in Japan 22 May 1981)