A New Synthesis of 3-Hydroxyfurans. The Reaction of Sulfonium Ylids with Ketene Dimer

Hisashi TAKEI, Moriaki HIGO, Kunio SAITO and Teruaki MUKAIYAMA

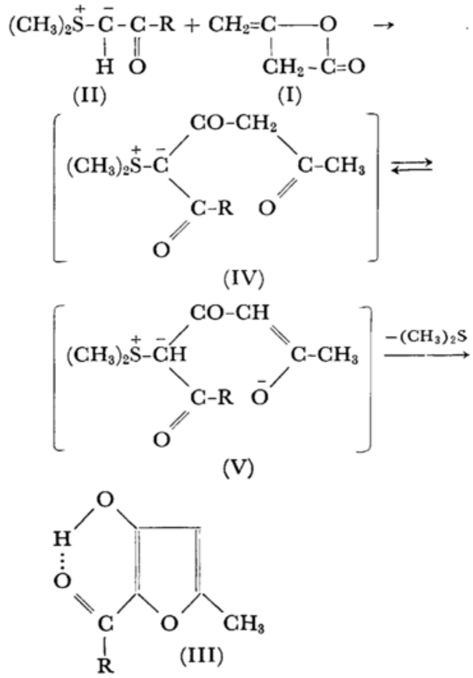
Laboratory of Organic Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

(Received April 25, 1968)

This communication reports a convenient method for the synthesis of 3-hydroxyfuran derivatives, structurally resemble to isomaltol which is obtained from lactose,1) by the reactions of ketene dimer (I) and some stabilized ylids. A typical run was as follows; ketene dimer was added to a dry benzene solution of dimethylsulfonium *p*-bromophenacylid (IIa) at room temperature under nitrogen. When the solution was refluxed for a short time, evolution of dimethyl sulfide was observed by its characteristic odour. After removal of the solvent, a resulting yellow precipitate was purified by a silica gel column to afford slightly yellow crystals, 2-(*p*-bromo benzoyl)-3-hydroxy-5-methylfuran (IIIa).2)

Similarly, 2-(*p*-substituted benzoyl)-, 2-acetyl-, 2-ethoxycarbonyl- and 2-diethylcarbamoyl-3-hydroxy-5-methylfurans were successfully synthesized by the reactions of the ylids, IIb-d, IIe, IIf and IIg, with ketene dimer in high yields. The results are summarized in Table 1.

The reaction can be considered to proceed through an initial formation of dimethylsulfonium acetoacetyl-(acyl)-methylid (IV) from II and I. The ylid IV, subsequently, is transformed into its tautomeric structure (V), which, on heating, decomposes to give III and dimethyl sulfide by an intramolecular nucleophilic displacement as shown below.



In conclusion, it is noted that this method enables to convert ketene dimer into 3-hydroxyfuran derivatives accompanied with ring expansion by the so-called methylene transfer.

TABLE 1. 3-HYDROXYFURANS BY THE REACTIONS OF STABILIZED SULFONIUM YLIDS WITH KETENE DIMER

Compd.	R in III	Method of ylid prepn.	Reaction time a) min	Yield %	Mp °C	Anal %					
						Found			Calcd		
						C	H	N	C	H	N
IIIa	$-C_6H_4-Br(p)$	A b)	30	83	84—86	51.59	3.28		51.27	3.23	
IIIb	$-C_6H_5$	A	40	99	57—59	71.57	4.99		71.28	4.99	
IIIc	$-C_6H_4-CH_3(p)$	A d)	20	87	49—52	71.93	5.33		72.21	5.59	
IIId	$-C_6H_4-OCH_3(p)$	B c,d)	40	91	62.5—64	66.69	5.06		67.23	5.21	
IIIe	$-CH_3$	B d)	45	81	93.5—95	60.08	6.04		59.99	5.75	
IIIf	$-OC_2H_5$	B	60	60	49—50	56.59	5.93		56.46	5.92	
IIIg	$-N(C_2H_5)_2$	B	20	47	52—54	61.05	7.51	7.08	60.89	7.67	7.10

a) All reactions were carried out in refluxing benzene.
b) Method A; ylids were prepared according to the method of Trost.3)
c) Method B; ylids were prepared according to the method of Payne.4)
d) These ylids were newly prepared from the corresponding sulfonium bromides.
Satisfactory elemental analyses were obtained.

---

1) B. E. Fisher and J. E. Hodge, *J. Org. Chem.*, **29**, 776 (1964), and references cited therein.

2) The structural assignment was made on the basis of analytical data, and IR and NMR spectrum.

3) B. M. Trost, *J. Am. Chem. Soc.*, **89**, 138 (1967).

4) G. B. Payne, *J. Org. Chem.*, **32**, 3351 (1967).