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2-Hydroxy-3-oxo-2,3-dihydrofuran-2-carboxylic Ester: The Oxidation Product of 3-Hydroxyfuran-2-carboxylic Ester

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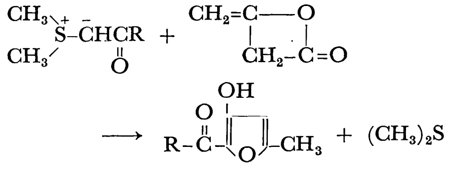
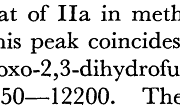
In a preceding communication,[1] it was shown that carbonyl-stabilized sulfonium ylides reacted with ketene dimer to give 2-acyl-3-hydroxy-5-methylfurans in good yields. For example, the reaction of ethyl dimethylsulfuranilideneacetate with ketene dimer in THF in an atmosphere of nitrogen afforded ethyl 3-hydroxy-5-methylfuran-2-carboxylate (Ia), mp 49—50°C, in a 60% yield. In this case, the furan was purified by distillation and analytical sample was obtained by subsequent sublimation.



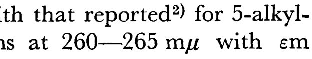
Ia $R=OC_2H_5$
b $R=C_6H_5$
c $R=CH_3$

It was found by the present experiment that when the reaction mixture was chromatographed over silica gel, colorless needles (IIa), mp 102—103°C, were isolated instead of Ia. Elemental analyses showed that IIa might be an oxidized product of Ia. Therefore, it is suggested that Ia was oxidized in the course of process for purification. Indeed, it was also found that the repetition of recrystallization from petroleum ether or the exposure of crystalline Ia to air for a long time resulted in the formation of IIa by air oxidation.

The structure of IIa was assigned to be ethyl 2-hydroxy-5-methyl-3-oxo-2,3-dihydrofuran-2-carboxylate, which is thought to be a cyclic hemiketal of III, on the basis of UV, NMR and IR spectra.



IIa $R=OC_2H_5$
b $R=C_6H_5$
c $R=CH_3$



$C_2H_5O\text{-}\overset{\displaystyle O}{\underset{}{C}}$ — $C_2H_5O\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}CH{=}\underset{\underset{\displaystyle HO}{|}}{C}\text{-}CH_3$

III

The UV spectrum of Ia in methanol showed a single peak at 265 mμ with εm 18000. Whereas, that of IIa in methanol gave εm 9200 at 269 mμ. This peak coincides with that reported[2] for 5-alkyl-3-oxo-2,3-dihydrofurans at 260—265 mμ with εm 8750—12200. The NMR spectrum has a singlet at 7.68 τ (3H, methyl), a triplet at 8.70 τ and a quartet at 5.65 τ (3H and 2H, ethyl ester) and a singlet at 4.43 τ (2H, furan nuclear proton and hydroxy proton). The last signal may be inadvertently superposed upon each other. The IR spectrum in KBr showed a band at 3170 cm^{-1} which suggested the presence of hydrogen bonding hydroxyl and three bands in carbonyl region at 1760, 1700 and 1600 cm^{-1} due to the carbonyl of five membered ring, hydrogen bonded ester carbonyl

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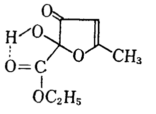
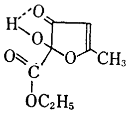
[1] H. Takei, M. Higo, K. Saito and T. Mukaiyama, This Bulletin, **41**, 1738 (1968).

[2] R. E. Rosenkranz, K. Allner, R. Good, W. V. Philisborn and C. H. Eugster, *Helv. Chim. Acta*, **46**, 1259 (1963).

and carbon–carbon double bond, respectively. Whereas IIa in methylene chloride solution gave three peaks in carbonyl region at 1740, 1720 and 1600 cm^{-1} attributable to hydrogen bonded carbonyl, ester carbonyl and carbon–carbon double bond, respectively. These facts suggest that the IIa may exist as IIa′ in crystalline, whereas IIa″ in solution.



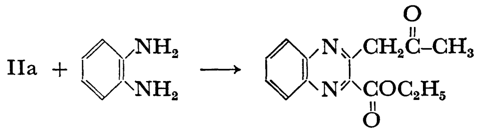
IIa′



IIa″

On the other hand, it was found that analogous furans such as Ib, the methyl ether of Ib, and Ic were stable towards air oxidation. Then these furans were treated with various oxidizing agents in order to obtain IIb and IIc. But, all attempts were unsuccessful and in the cases of Ib and of its methyl ether, benzoic acid was obtained as a main product.

Finally the reaction of IIa was tried with the expectation that it would be used as a useful intermediate in the field of synthetic chemistry. When IIa was allowed to react with *o*-phenylenediamine, ethyl 3-(2-oxopropyl)quinoxaline-2-carboxylate (IV) was obtained in a 69% yield.[3)]



IV

Experimental

Reaction of Ethyl Dimethylsulfuranilideneacetate with Ketene Dimer. a) To a solution of ethyl dimethylsulfuranilideneacetate (1.48 g, 0.01 mol) in THF, ketene dimer (0.84 g, 0.01 mol) in the same solvent was added dropwise under ice cooling in an atmosphere of nitrogen. The reaction mixture was allowed to stand at room temperature for an hour and then was refluxed for 20 min. After removal of the solvent, the resulting dark brown syrup was distilled to give crude Ia (1.00 g, 60%), bp 80—90°C/2 mmHg, which solidified immediately. The analytical sample was obtained by the subsequent sublimation under reduced pressure, mp 49—50°C.

Found: C, 56.59; H, 5.93%. Cacld for $C_8H_{10}O_4$: C, 56.46; H, 5.92%.

b) When the dark brown syrup in the above experiment was submitted to silica gel column chromatography, semi-crystalline material was eluted by benzene - methylene chloride. The crystals were collected and recrystallized twice from cyclohexane with small amount of benzene to give colorless needles, IIa, (0.62 g, 33%) mp 100—103°C.

Found: C, 51.72; H, 5.25%. Calcd for $C_8H_{10}O_5$: C, 51.61; H, 5.41%.

Reaction of IIa with *o*-Phenylenediamine. A mixture of IIa (0.19 g, 0.001 mol), *o*-phenylenediamine (0.11 g, 0.001 mol) and two drops of acetic acid in ethanol was kept at room temperature for 2 days. After evaporation of the solvent, the residue was submitted to preparative thinlayer chromatography. When it was developed by ethyl acetate, pale orange crystals, IV, were obtained from the part of R_f value about 0.7—0.85, which were recrystallized from dilute alcohol, mp 86—87.5°C (0.18 g, 69%). The infrared spectrum (KBr) showed strong absorptions at 1740 (ester carbonyl) and at 1720 cm^{-1} (ketone).

Found: C, 64.87; H, 5.46; N, 10.92%. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.10; H, 5.46; N, 10.85%.

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3) In this connection, Lutz *et al.* have reported that 2-hydroxy-3-oxo-2,3-dihydrofuran, hemiketal of enol form of 1,2,4-triketone, reacts with *o*-phenylenediamine to give quinoxaline derivative. R. E. Lutz and A. H. Stuart, *J. Amer. Chem. Soc.*, **58**, 1885 (1936), and references cited therein, See, also J. C. E. Simpson, "The Chemistry of Heterocyclic Compounds. Condensed Pyridazine and Pyrazine Rings," Interscience Publishers Inc., New York (1953), p. 293.