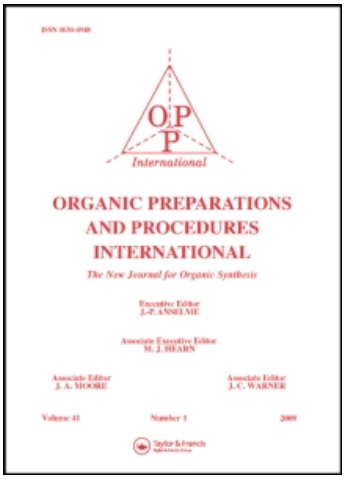

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

SYNTHESIS OF 3-ACETOACETYL-7-METHYL-2H,5H-PYRANO[4,3-B]PYRAN-2,5-DIONE

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To cite this Article Boutemeur-Kheddis, B. , Bendaas, A. , Hamdi, M. , Sakellariou, R. and Spéziale, V.(1994) 'SYNTHESIS OF 3-ACETOACETYL-7-METHYL-2H,5H-PYRANO[4,3-B]PYRAN-2,5-DIONE', Organic Preparations and Procedures International, 26: 3, 360 — 362
To link to this Article: DOI: 10.1080/00304949409458438
URL: http://dx.doi.org/10.1080/00304949409458438

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SYNTHESIS OF

3-ACETOACETYL-7-METHYL-2H,5H-PYRANO[4,3-b]PYRAN-2,5-DIONE

Submitted by (07/13/93)

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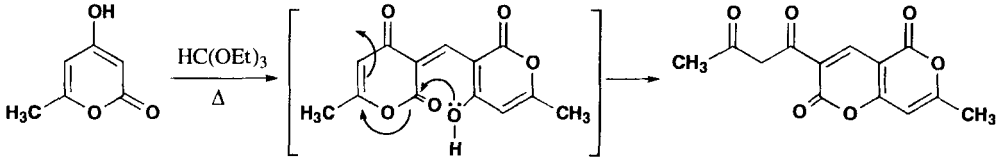
In the course of a study of pyrone derivatives, we were interested in the synthesis of 6-methyl-3-(4-hydroxy-6-methyl-2-one-2H-pyran-3-yl) methylene-2,4 (3H)-pyran-2,4-dione (**1**). Selective catalytic hydrogenation of this compound would lead to the derivative prepared by another method, and would also serve as reference for the identification of a secondary product formed in various other reactions under the investigation.[1] The only reported method is that of Hirsh and Hoefgen[2] who obtained **1** by heating 4-hydroxy-6-methyl-2-pyrone with ethyl orthoformate in either

toluene in the presence of pyridine or piperidine, or in benzene in the presence of triethylamine. No spectroscopic study was reported and the authors listed only melting point and yields.



1 2

Using the conditions described by these authors, or in methanoi or ethanol in the absence of base, we obtained a single product whose color was found to depend on the method of synthesis. However, all compounds had melting points identical to that of the compound described by Hirsh and Hoefgen. These observations were consistent with the existence of several possible structures. However, the compounds had identical NMR spectra determined at 300 MHz in $CDCl_3$, but analysis of the spectrum indicated that the structure differed by the presence of a CH_2 group from that proposed by Hirsh and Hoefgen and showed the presence of an acetoacetyl group which was characterized from singlets at δ 2.40 (CH_3), 4.11 (CH_2, diketo form), 8.76 (CH, enol form) and a broad singlet at δ 15.74 from the OH proton of the enol form. The existence of the acetoacetyl group was further supported by the presence of a signal at δ 56.62 in ^{13}C NMR, resonating as a triplet in the coupled spectrum, and corresponding to the carbon atom in the CH_2 group of the dione form of the acetoacetyl group. Mass spectrometry showed peaks at 177, 205, 219, and 247 characteristic of an acetoacetyl group due to loss of the $COCH_2COCH_3$, CH_2COCH_3, $COCH_3$ and CH_3 fragments. These results were compared with those obtained for the compound with a partially similar skeleton, 3-acetoacetylcoumarin.[3] To lend further support to our proposed structure, one of the yellow compounds was examined by X-ray crystallography.[4] This showed the presence of an acetoacetyl group, and confirmed that the derivative synthesized was 3-acetoacetyl-7-methyl-2H,5H-pyrano[4,3-b]pyran-2,5-dione (**2**). Its formation can be accounted for by intramolecular translactonization of 6-methyl-3-(4-hydroxy-6-methyl-2-one-2H-pyran-3-yl)methylene-2,4(3H)-pyran-2,4-dione (**1**) similar that described for analogous compounds.[5]

EXPERIMENTAL SECTION

Melting points were determined in an Electrothermal apparatus. ^1H NMR and ^{13}C NMR and mass spectra were recorded on a Bruker AC 80, Bruker WM 300 and instrument Nermag 1010 instruments respectively. The elemental analysis was carried out at the Inter-University microanalysis center in Toulouse.

Synthesis of Compound (2).- A stirred solution of 4-hydroxy-6-methyl-2-pyrone (2.52 g, 0.02 mole), ethyl orthoformate (9 mL) in 30 mL of ethanol was refluxed for 4 hrs. The precipitate was collected and recrystallized from toluene (3.67 g, 70%), mp. 192-193°; ^1H NMR ($CDCl_3$): δ 2.23 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 4.11 (s, 2H, CH_2), 6.23 (m, 1H, CH), 6.61 (s, 1 H, CH), 8.76 (s, 1 H, CH), 15.74 (s,

1 H, OH). ^{13}C NMR ($CDCl_3$): δ 21.08, 27.52, 56.62, 98.94, 100.98, 101.71,116.0, 142.75, 156.10, 159.27, 167.13, 168.50, 171.19, 199.50. MS m/z (relative abundance): 262 (M^+, 32), 247 (14), 219 (6), 205 (100), 150 (8), 95 (11), 84 (6), 69 (25), 67 (5), 57 (9).

Anal. Calcd. for $C_{13}H_{10}O_6$: C, 59.54; H, 3.82. Found: C, 59.55; H, 3.56

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A NEW APPROACH TO ALKYL 2-OXOQUINOLINE-3-ACETATES BY TRIPHENYLPHOSPHINE-INDUCED CYCLIZATION OF ALKYL *o*-FORMYLMALEANILATES†

Submitted by (07/13/93)

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Suitably *ortho*-substituted maleanilic acids and their derivatives are useful for the synthesis of a variety of heterocyclic skeletons of structural[1] and biological interest.[2] We now report an application of alkyl *o*-formylmaleanilates (**9c-f**) for the synthesis of quinoline derivatives (**10c-f**). Maleic anhydride (**1**) reacts with triphenylphosphine (TPP) to generate triphenylphosphoranylidene succinic anhydride (**4**),[3] while maleimides (**2**) and isomaleimides (**3**) yield triphenylphosphoranylidene succinimides (**5**).[3] These phosphoranes have been used for syntheses of butenolides,[4] furans,[5] intermediates