The Reaction of 6-Carboxymethyl-4-methoxy-2-pyrone with Acetic Anhydride

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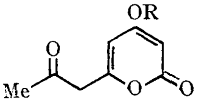
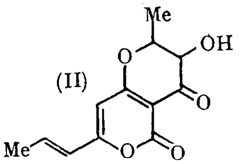
THE isolation of tetra-acetic lactone (I; R = H), which is regarded as a precursor of radicinin (II) as well as a masked β-trioxo-carboxylic acid, and its recyclization to orcinol are of biogenetic interest.[1,2] We report the reaction of 6-carboxymethyl-4-methoxy-2-pyrone with acetic anhydride.[3]

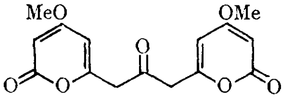
With acetic anhydride in pyridine at room temperature (4 hr.), 6-carboxymethyl-4-methoxy-2-pyrone gave (45%) of tetra-acetic lactone methyl ether (I; R = Me) [m.p. 80—81°, δ_{Me_4Si} ($CDCl_3$) 2·26 (3H, s), 3·54 (2H, s), 3·81 (3H, s), 5·45 (1H, d, J 2 c./sec.), and 5·93 p.p.m. (1H, d, J 2 c./sec.)], which could be recyclized to 2,6-dihydroxy-4-methoxyacetophenone with base, in addition to the enol acetate of (III), m.p. 163—164° (10%) and the oxodipyrone (III) (4%); the latter was converted to its enol acetate with acetic anhydride in pyridine or isopropenyl acetate.† On heating 6-carboxymethyl-4-methoxy-2-pyrone with acetic anhydride and sodium acetate (100°, 4 hr.),[4] a low yield of the enol acetate of (III) was also obtained. On being heated with acetic anhydride in pyridine (100°, 4 hr.), 6-carboxymethyl-4-methoxy-2-pyrone did not, however, give tetra-acetic lactone methyl ether, but instead an unexpected diacetyl pyrone (IV) [25%, m.p. 145—146°, *m/e* 224, δ_{Me_4Si} ($CDCl_3$) 2·15 (6H, s), 3·87 (3H, s), 5·51 (1H, d, J 2 c./sec.) and 5·96 p.p.m. (1H, d, J 2 c./sec.)], which was hydrolyzed to (I; R = Me) with 50%-H_2SO_4. Treatment of (I; R = Me) with acetic anhydride in pyridine (100°, 4 hr.) also gave (IV) (40%).



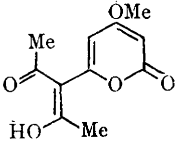
(I) R=H or Me



(II)



(III)



(IV)

The easy formation of (I) will be useful in biosynthetic experiments on natural substances having tetra-acetic lactone as a precursor in their biosyntheses. All compounds gave satisfactory physical data.

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[1] R. Bentley and P. M. Zwitkowits, *J. Amer. Chem. Soc.*, 1967, **89**, 676.

[2] J. F. Grove, *J. Chem. Soc.*, 1964, 3234.

[3] J. L. Douglas and T. Money, *Canad. J. Chem.*, 1968, **46**, 695.

[4] Recently, the synthesis of the enol acetate of (III), from which xanthone was formed by base, has been reported (D. G. Pike, J. J. Ryan, and A. I. Scott, *Chem. Comm.*, 1968, 629).

† These reaction products were separated by silica gel chromatography (Mallinckrodt, 100 Mesh). In this case, the enol acetate of (III) may be converted to (III) by silica gel–$CHCl_3$.