# 2,3-Dihydro-2-alkyl-7-methyl-4H,5H-pyrano(4,3-b)pyran-4, 5-diones from the Reaction of Dehydroacetic Acid and Aldehydes.

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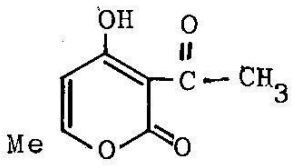
In the course of our synthetic studies we have found some interesting cyclisation reactions. The base catalysed condensation of dehydroacetic acid (1) with aromatic or aliphatic aldehydes has been reported [1-3] to give substituted 3-cinnamoyl or 3-α,β-unsaturated acyl-4-hydroxy-6-methyl-2H-pyran-2-one (II). On the contrary, under the similar condition we have found the formation of 2,3-dihydro-2-alkyl-7-methyl-4H,5H-pyrano (4,3-b)pyran-4,5-diones (III) from the reaction of aliphatic aldehydes with dehydroacetic acid. The cyclised products (III) are of synthetic importance because they have the same pyrano-pyrandione nucleus as that of radicinin [4], a phytotoxic metabolite of the carrot plant pathogen Stemphylium radicinum.



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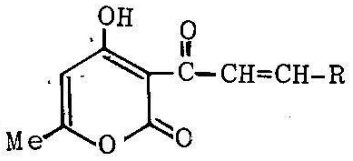
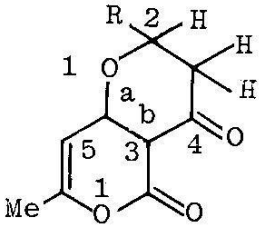


| II | R |
|---|---|
| a | $CH(CH_3)_2$ |
| b | CH=CH-Ph |
| c | Ph |
| d | P-MeO-Ph |



| III | R |
|---|---|
| a | $CH_2-CH_2-Ph$ |
| b | $CH(CH_3)_2$ |
| c | $CH_2CH_2CH_3$ |

A solution of dehydroacetic acid (0.025 mole), phenyl-propionaldehyde (0.02 mole) in chloroform (30 ml) containing pirperidine (0.5 ml) was refluxed (6-8 hrs.) and the water formed during the reaction was continuously removed by azeotropic distillation. Removal of solvent left a yellow residues which was chromatographed on silica gel (20 g.) with chloroform-benzene (3.2) as eluent. The fractions afforded 2,3-dihydro-7-methyl-2-phenethyl-4H,5H-pyrano-(4,3-b)pyran-4,5-dione (IIIa, 45%). m.p. 145-147°C (Found: C,71.97; H, 5.79, $C_{17}H_{16}O_4$ requires C, 71.83; H, 5.63%); $\nu_{max}$ (nujol) 1745 (CO of α-pyrone) and 1659 $cm^{-1}$ (CO γ-pyrone);

nmr ($CDCl_3$) δ 2.25, 3H of methyl (7); 2.08 2H methylene (3); 2.7, 4H of two methylene (2); 4.6, 1H (2); 5.9 1H allylic (8); 7.24, 5H aromatic (2).

Reaction of isobutyraldehyde with (1) under the same conditions afforded dihydropyranopyrandione (IIIb). m.p. (pet.ether-$CHCl_3$) 178-180°C; $\nu_{max}$ 1750(CO of α-pyrone) and 1658 $cm^{-1}$ (CO of γ-pyrone). (Found: C, 65.0; H, 6.3, $C_{12}H_{14}O_4$ requires C, 64.8; 6.30%); nmr ($CDCl_3$) δ 1.05, 6H of 2Me (2); 2.0, 2H methylene (3); 4.37, 1H (2), 2.24, 3H of methyl (7); 5.88, 1H allylic (8). The spectral data is in agreement with the product obtained by Marcus et al.[5] but at variance with the product (IIa) m.p. 178.5-181.3°C claimed by Kimura et al. [3] in a similar reaction.

Butyraldehyde under the corresponding condition yielded (IIIc) m.p. 160-163°C. The product was characterised on the basis of elemental analysis and spectral data.

A similar reaction of cinnamaldehyde with dehydroacetic acid (1) gave (IIb) in 54% yield, m.p. (ethanol-$CHCl_3$) 161-162°C (Found: C, 72.37, H, 4.73 $C_{17}H_{14}O_4$ requires C, 72.34; H, 4.96%). $\nu_{max}$ (nujol) 1720 (CO of α-pyrone) and 1638 $cm^{-1}$ (CO,H-bonded at 3-position) $\lambda_{max}$ (ethanol) 380 nm (ε 24483), 263 n.m. (ε 14827) nmr ($CDCl_3$) 2.24, 3H of Me (6); 4.1, 1H adj. to CO of side chain (3) 5.9, 1H allylic (5), 7.0-7.8, 8H of side chain including the Ph (3); 18.2, 1H enolic (4). Analogous reactions of benzaldehyde and p-methoxy-benzaldehyde with (1) also gave 3-cinnamoyl derivatives (IIc) m.p. 129-130°C (lit. [2] m.p. 130-132°C) and (IId) m.p. 170°C respectively.

From these reactions it may be concluded that the formation of dihydropyranopyran-diones (III) involves the cyclisation of the initially formed condensation products (II,R=$CH_2$-ph, $-CH(CH_3)_2$, $-CH_2-CH_2-CH_3$) via internal Michael type reaction. The failure of similar cyclisation reaction in case of cinnamoyl derivative (IIb,c,d) is attributable to the conjugative effect of the phenyl group. This fact is substaintiated by the results of the present investigation. The method provides a convenient route for the synthesis of pyranopyran-diones which consitute the nucleus of the radicinin molecule.

## References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