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AN UNUSUAL REACTION OF DIMEDONE WITH ACID ANHYDRIDES

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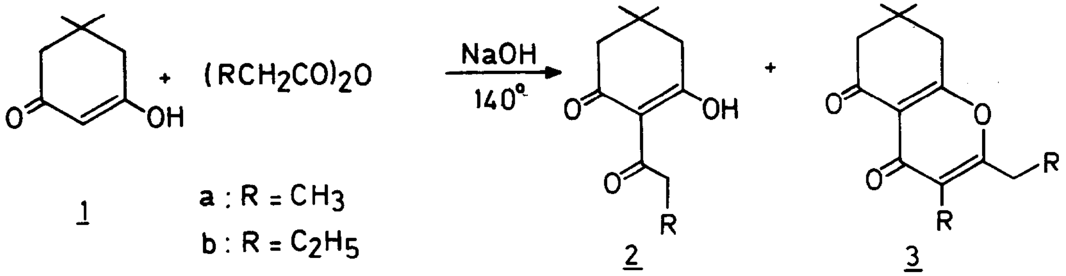
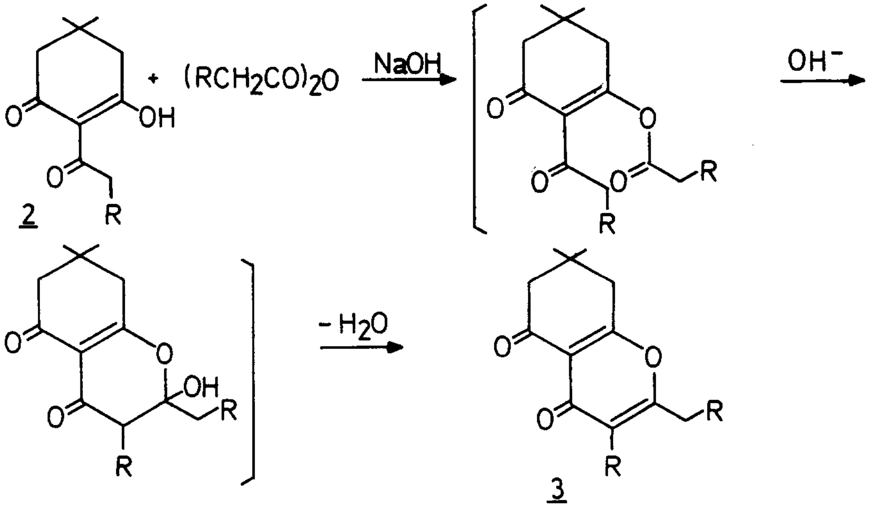
2-Acyl-1,3-cyclohexanediones have been prepared by reaction of 1,3-cyclohexanediones with an excess of acid anhydrides in the presence of a catalytic amount of sodium acetate(1,2) or boron trifluoride(3). In the course of our studies on the synthetic reactions of 1,3-cyclohexanediones(4,5), it has been found that during the acylation of dimedone (1) with anhydrides by-products 3 could be isolated next to the expected 2-acyldimedones (2).



The reaction of dimedone (1) with propionic anhydride at 140° in the presence of sodium hydroxide gave 19 % 2-propionyldimedone (2a) and 50 % of a cristalline compound which was identified as 2-ethyl-5,6,7,8-tetrahydro-3,7,7-trimethyl [4H]benzopyran-4,5-dione (3a); m.p. 152°; U.V. (methanol) 222 (12,100) 254 (2,350). N.M.R. ($CDCl_3$) : 1.13 (6H, s, $2xCH_3$), 1.23 (3H, t, J 7.5 Hz, CH_2CH_3), 1.92 (3H, s, $=-CH_3$), 2.39 (2H, s, CH_2), 2.63 (2H, q, J 7.5 Hz, CH_2CH_3), 2.73 (2H, s, CH_2). The I.R. spectrum showed the typical pattern of a γ-pyrone ring : two carbonyl functions at 1700 and 1650 cm^{-1} and two bands of conjugated double bonds at 1625 and 1575 cm^{-1}. The mass spectrum exhibited the M^+ (m/e : 234) as the most abundant ion besides the ion m/e 178 resulting from a retro-Diels-Alder fragmentation of the pyrone ring.

Reaction of dimedone (1) with n.butyric anhydride gave only 9 % 2-butyryldimedone (2b) but 60 % of 3-ethyl-5,6,7,8-tetrahydro-7,7-dimethyl-2-propyl [4H]benzopyran-4,5-dione (3b); m.p. 102°; U.V. (methanol) 227, 254 nm; I.R. (KBr); 1700 and 1655 (CO); 1625 and 1575 cm^{-1} (C=C); N.M.R. ($CDCl_3$) : 1.01 (3H, t, J 7.1 Hz, CH_3), 1.05 (3H, t, J 7.1 Hz, CH_3), 1.15 (6H, s, 2xCH_3), 1.72 (2H, sextet, J 7.1 Hz, CH_2), 2.39 (2H, s, CH_2), 2.40 (2H, q, J 7.1 Hz, $=\!-CH_2-CH_3$), 2.59 (2H, t, J 7.1 Hz, $=\!-CH_2-$), 2.73 (2H, s, CH_2) ; m/e : 262(21), 247(100).

The formation of the pyrone derivatives 3 can be explained by O-acylation of the initially formed 2-acyldimedones 2 followed by an intramolecular base-catalyzed aldol cyclization.



However, reaction of dimedone with acetic anhydride gave 79 % 2-acetyldimedone and 3 % of the anhydride of 2-acetyldimedone, but no pyrone compounds were isolated .

Treatment of the pyrones 3 with 20 % sodium hydroxide resulted in ring opening with formation of the corresponding 2-acyldimedones 2.

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