REACTION OF CYCLIC β-KETOALCOHOLS WITH TRITYL PERCHLORATE

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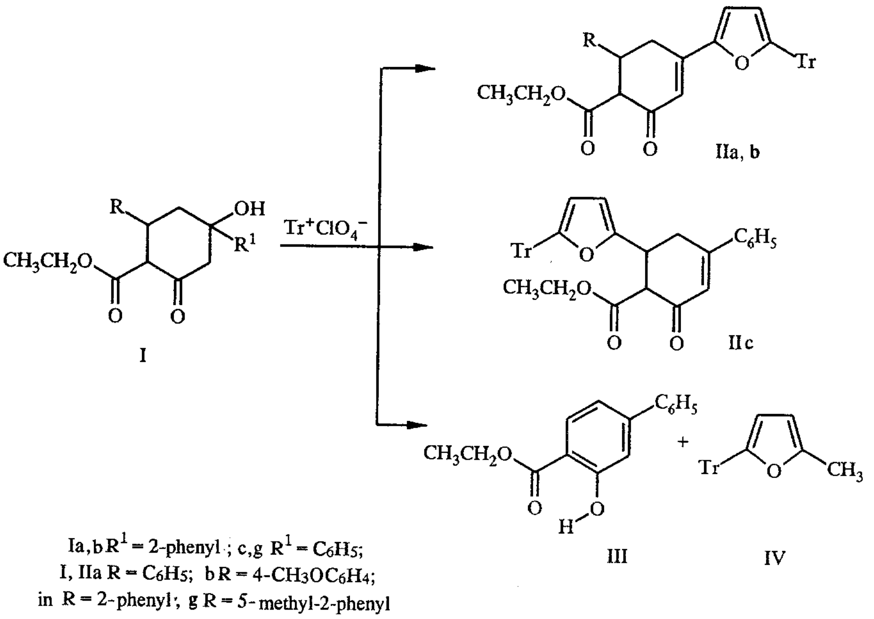
It has previously been reported [1] that 5-furyl-β-cyclohexanones Ic, d readily undergo aromatization on acid catalysis with splitting off of furan (or sylvan) and formation of salicyclic acid derivatives. We tried to aromatize compounds Ia-d while retaining all the substituents in the ring, using trityl perchlorate as an effective hydride ions acceptor [2, 3]. Our experiments showed that the reaction of compounds Ia-d with trityl perchlorate ($TrClO_4$) proceeds without splitting off of hydride ion from the nonaromatic carbocyclic ring:



Ia,b R^1 = 2-phenyl ; c,g R^1 = C_6H_5;
I, IIa R = C_6H_5; b R = 4-$CH_3OC_6H_4$;
in R = 2-phenyl·, g R = 5-methyl-2-phenyl

In the case of compounds Ia-c containing a 5-unsubstituted furan ring, the trityl group substitutes hydrogen at the 5-position of the furan ring, while the thus liberated perchloric acid catalyzes the dehydration with the formation of compounds IIa-c. In the presence of a substituent in the 5-position of the furan ring (compound IId), trityl perchlorate acts as a 5-methylfuran ring "acceptor," which finally leads to the previously described [1] ethyl ester of p-phenylsalicyclic acid III and triphenyl(5-methyl-2-furyl)methane IV.

5-Phenyl-3-(5-triphenylmethyl-2-furyl)-6-ethoxycarbonyl-2-cyclohexen-1-one (IIa, $C_{38}H_{32}O_4$), mp 218-220°C. IR spectrum (Nujol), cm^{-1}: 1600, 1640, 1720. PMR spectrum (60 MHz, acetone-D_6), ppm: 0.93 (3-H, t, CH_3CH_2CO, J = 7.2 Hz), 2.80 (2H, m, 4-H_a and 4-H_e), 3.50 (2H, q, CH_3CH_2CO), 3.62 (2H, m, 5-H and 6-H), 6.12 (1H, d, 4-H_{furan}, J = 3.6 Hz), 6.27 (1H, d, 2-H), J = 2.0 Hz), 6.73 (1H, d, 3-H_{furan}), 7.17 (15H, m, $C(C_6H_5)_3$), 7.25 (5H, s, C_6H_5).

5-(4-Methoxyphenyl)-3-(5-triphenylmethyl-2-furyl)-6-ethoxycarbonyl-2-cyclohexen-1-one (IIb, $C_{39}H_{34}O_5$), mp 214-216°C. IR spectrum (Nujol), cm^{-1}: 1600, 1650, 1720. PMR spectrum (60 MHz, acetone-D_6), ppm: 1.1 (3-H), t, CH_3CH_2CO, J = 7.1 Hz), 2.75 (1H, m, 4-H_a) 2.80 (1H, m, 4-H_e), 3.50 (2H, m, 5-H and 6-H), 3.52, (2H, q, CH_3CH_2CO), 3.65 (3H, s,

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CH_3O), 6.07 (1H, d, 4-H_{furan}, J = 3.6 Hz), 6.28 (1H, d, 2-H, J = 2.0 Hz), 6.58 (1H, d, 3-H_{furan}), 6.70 (2H, d, 2-H and 6-H of the benzene ring), 7.10 (2H, d, 3-H and 5-H of the benzene ring), 7.17 (15H, m, $C(C_6H_5)_3$), 7.27 (5H, s, C_6H_5).

3-Phenyl-5-(5-triphenylmethyl-2-furyl)-6-ethoxycarbonyl-2-cyclohexen-1-one (IIb, $C_{38}H_{32}O_4$), mp 153-155°C. IR spectrum (Nujol), cm^{-1}: 1600, 1640, 1720. PMR spectrum (60 MHz, acetone-D_6), ppm: 1.10 (3-H, t, CH_3CH_2CO, J = 7.2 Hz), 2.95 (2H, m, 4-H_a and 4-H_e), 3.63 (2H, m, 5-H and 6-H), 4.02 (2H, q, CH_3CH_2CO), 5.83 (1H, d, 4-H_{furan}, J = 3.6 Hz), 6.03 (1H, d, 3-H_{furan}), 6.35 (1H, d, 2-H, J = 2.0 Hz), 7.12 (15H, m, $C(C_6H_5)_3$), 7.35 (5H, s, C_6H_5).

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